Supporting Information

A Simple *N*-Heterocyclic Carbene for the Catalytic Up-conversion of Aldehydes into Stoichiometric Super Electron Donors

Nadhrata Assani,[a] Ludivine Delfau,[b] Preslav Smits,[b] Sébastien Redon,[a] Youssef Kabri,[a] Eder Tomás-Mendivil,[b] Patrice Vanelle,[a] David Martin*[b] and Julie Broggi*[a]

[a] Aix Marseille Univ, CNRS, ICR, Institut de Chimie Radicalaire - UMR 7273, Faculté de Pharmacie, 13005, Marseille, France
[b] Univ. Grenoble-Alpes, CNRS, UMR CNRS-UGA 5250, CS 40700, 38058 Grenoble, France

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1. General considerations

For starting materials and catalysis products: The reactions were performed -*unless otherwise noted*- in an MBraun glovebox containing dry argon and less than 1 ppm of oxygen. The following adsorbent was used for column chromatography: silica gel 60 (Merck, particle size 0.063-0.200 mm, 70-230 mesh ASTM). TLC was performed on 5 cm × 10 cm aluminum plates coated with silica gel 60F-254 (Merck) using an appropriate eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at ambient temperature in solutions of $CDCl_3$ (δH = 7.26 ppm and δC = 77.16 ppm) or DMSO-d_6 (δH = 2.50 ppm and δC = 39.52 ppm). Chemical shifts are given in ppm, coupling constants "*J*" are expressed in Hertz (multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet). HRMS and elemental analyses were carried out at the Spectropole, Faculté des Sciences et Techniques de Saint-Jérôme, Marseille.

1,1'-Ethenylidenebis[4-methylbenzene][1], 4,4'-(Ethene-1,1-diyl)bis(methoxybenzene)[2], 4-(1-Phenylvinyl)pyridine[3], 2-(1-Phenylvinyl)pyridine[4], 2-(1-Phenylethenyl)thiophene[5] were prepared according to reported procedure. Other reagents and extra dry solvents were purchased from commercial suppliers and used as received.

For acyl azolium salts: The synthesis and characterization of acyl azolium salts were performed -*unless otherwise noted*- under an atmosphere of dry argon using standard Schlenk or glovebox techniques. Solvents were dried by standard methods (Na for ethers and toluene, and CaH_2 for the rest) and distilled under argon. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on the NMR-ICMG platform of Grenoble with Bruker Avance 400 and 500 MHz spectrometers at 298 K. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F). Coupling constants "*J*" are given in Hertz as positive values. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Melting points were measured with a Büchi B-545 melting point apparatus system. Mass spectra were recorded on a Waters Gevo X2-S Qtof mass spectrometer or on a Thermo Scientific LTQ Orbitrap XL mass spectrometer.

1,3-Dimethylimidazolium iodide[6], 1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate[7], 2,6-diisopropylphenyl (Dipp)[8] *N*-substituted thiazolium salts, 1,3-diisopropylimidazolium tetrafluoroborate[9], 1,3-Bis(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate[10] and 1,3-Dimethyl-1*H*-benzimidazolium iodide[11] were prepared according to reported procedure. Benzoyl chloride was purified according to a reported procedure[12]. Other starting materials were purchased from commercial sources and used without further purification.

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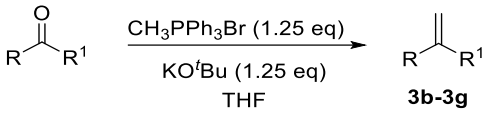
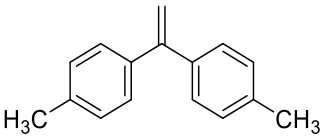
2. Synthesis and characterization of starting materials



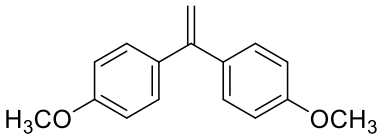
3b-3g

Procedure A: In a schlenck tube under argon atmosphere, a solution of potassium *tert*-butoxide (1.25 equiv., 6.25 mmol, 0.7 g) in dry THF (5 mL) was added dropwise to a solution of methyltriphenylphosphonium bromide CH_3PPh_3Br (1.25 equiv., 6.25 mmol, 2.23 g) in dry THF (10 mL) *via* a cannula at 0°C. The resulting mixture was stirred at room temperature for 1 hour. Then, a solution of the corresponding ketone (1 equiv., 5 mmol) in dry THF (10 mL) was added dropwise to the mixture and stirred for 48 hours at 50°C. Upon completion, the reaction was quenched with a saturated solution of ammonium chloride (NH_4Cl), and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum. Pentane was added to the crude and the mixture was stirred for 1 hour at r.t.. Then, the mixture was filtered and washed with pentane and solvent and volatiles were removed under vacuo. The desired product was purified by silica gel column chromatography.



1,1'-Ethenylidenebis[4-methylbenzene], 3b – [CAS : 2919-20-2] – $C_{16}H_{16}$
3b was synthesized following **procedure A** from 4,4'-dimethylbenzophenone (1 g) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ ethyl acetate 90/10 to 70/30) as a light orange solid (625 mg, 60%).

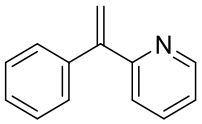
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.1 Hz, 4H), 7.15 (d, J = 8.1 Hz, 4H), 5.39 (s, 2H), 2.37 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.9 (C), 139.0 (2 x C^{Ar}), 137.6 (2 x C^{Ar}), 129.0 (4 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 113.1 (CH_2), 21.3 (2 x CH_3).
HRMS (ESI-MS) *m/z* calcd for $C_{16}H_{16}Ag^+$: 315.0297 $[M+Ag]^+$; found: 315.0296.
Spectral data agrees with the reported literature[1].



4,4'-(Ethene-1,1-diyl)bis(methoxybenzene), 3c – [CAS : 4356-69-8] – $C_{16}H_{16}O_2$
3c was synthesized following the **procedure A** from 4,4'-dimethoxybenzoph

enone (1.2 g) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 90/10) as a white solid (407 mg, 34%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (d, J = 8.9 Hz, 4H, H^{Ar}), 6.88-6.86 (d, J = 8.9 Hz, 4H, H^{Ar}), 5.30 (s, 2H, CH_2), 3.83 (s, 6H, 2 x OCH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4 (2 x C^{Ar}), 149.1 (C), 134.5 (2 x C^{Ar}), 129.6 (4 x CH^{Ar}), 113.6 (4 x CH^{Ar}), 111.8 (CH_2), 56.4 (2 x OCH_3).
Spectral data agrees with the reported literature[2].



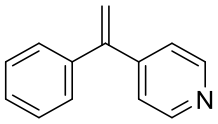
2-(1-Phenylvinyl)pyridine, 3d – [CAS : 15260-65-8] – $C_{13}H_{11}N$

3d was synthesized following **procedure A** from 2-benzoylpyridine (0.9 g) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 90/10) as a yellow oil (234 mg, 27%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H, H^{Ar}), 7.51 (td, *J* = 7.7, 1.9 Hz, 1H, H^{Ar}), 7.30-7.23 (m, 5H, H^{Ar}), 7.17 (dd, *J* = 7.9, 1.1 Hz, 1H, H^{Ar}), 7.09 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H, H^{Ar}), 5.92 (d, *J* = 1.4 Hz, 1H, C*H*-H), 5.51 (d, *J* = 1.5 Hz, 1H, CH-*H*).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5 (C^{Ar}), 149.4 (CH^{Ar}), 149.2 (C), 140.4 (C^{Ar}), 136.3 (CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 127.9 (CH^{Ar}), 122.9 (CH^{Ar}), 122.5 (CH^{Ar}), 117.8 (CH_2).

Spectral data agrees with the reported literature[4].



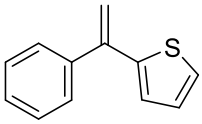
4-(1-Phenylvinyl)pyridine, 3f – [CAS : 54813-56-8] – $C_{13}H_{11}N$

3f was synthesized following **procedure A** from 4-benzoylpyridine (0.9 g) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 80/20) as a yellow oil (131 mg, 14%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 6.2 Hz, 2H, H^{Ar}), 7.35-7.33 (m, 3H, H^{Ar}), 7.29-7.27 (m, 2H, H^{Ar}), 7.22 (d, *J* = 6.2 Hz, 2H, H^{Ar}), 5.59 (d, *J* = 2.9 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.9 (2 x CH^{Ar}), 148.9 (C), 148.0 (C^{Ar}), 139.8 (C^{Ar}), 128.5 (2 x CH^{Ar}), 128.3 (CH^{Ar}), 128.2 (2 x CH^{Ar}), 122.8 (2 x CH^{Ar}), 117.0 (CH_2).

Spectral data agrees with the reported literature[3].



2-(1-Phenylethenyl)thiophene, 3g – [CAS : 30616-74-1] – $C_{12}H_{10}S$

3g was synthesized following **procedure A** from 2-benzoylthiophene (0.9 g) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 90/10) as a yellow oil (491 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 2H, H^{Ar}), 7.37-7.30 (m, 3H, H^{Ar}), 7.19 (dd, *J* = 5.1, 1.2 Hz, 1H, H^{Ar}), 6.95 (dd, *J* = 5.1, 3.6 Hz, 1H, H^{Ar}), 6.90 (dd, *J* = 3.7, 1.2 Hz, 1H, H^{Ar}), 5.58 (s, 1H, C*H*-H), 5.23 (s, 1H, CH-*H*).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9 (C^{Ar}), 143.6 (C^{Ar}), 141.2 (C), 128.4 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 128.2 (CH^{Ar}), 127.4 (CH^{Ar}), 126.6 (CH^{Ar}), 125.1 (CH^{Ar}), 113.7 (CH_2).

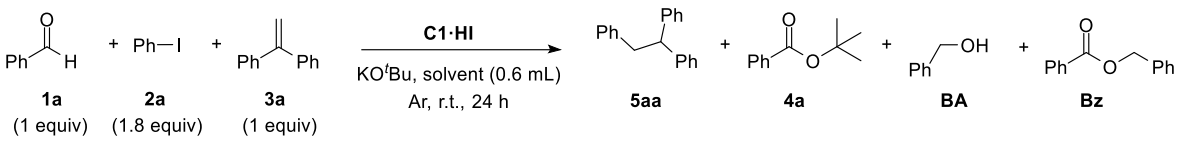
HRMS (ESI-MS) *m/z* calcd for $C_{12}H_{11}S^+$: 187.0576 $[M+H]^+$; found: 187.0574.

Spectral data agrees with the reported literature[5].

3. *NHC*-catalyzed oxidative process: scope of aldehydes

a. Complementary optimization reactions

Table S1 - Optimization of the reaction conditions – Part 1



1a (1 equiv) + **2a** (1.8 equiv) + **3a** (1 equiv) → **5aa** + **4a** + **BA** + **Bz**

Entry	Base	Solvent	^{1}H NMR conv. of 5aa (%)	4a (%)	Ratio of BA (%)	Bz (%)
1	KO^{t}Bu	MTBE	69	80	20	20
2	KO^{t}Bu	DMF	29	>99	n.o	n.o
3	NaO^{t}Bu	DMF	10	73	27	n.o
4	$NaNH_2$	DMF	22	n.o	<1	<1
5	Piperidine	DMF	n.o	n.o	n.o	n.o
6	DBU	DMF	n.o	n.o	n.o	n.o
7[a]	KO^{t}Bu	MTBE	45	>99	n.o	n.o
8[b]	KO^{t}Bu	MTBE	76	63	7	30
9[c]	KO^{t}Bu	MTBE	63	>99	n.o	n.o
10	KO^{t}Bu	MTBE[d]	49	>99	<1	n.o
11	KO^{t}Bu	MTBE[e]	63	96	3	1

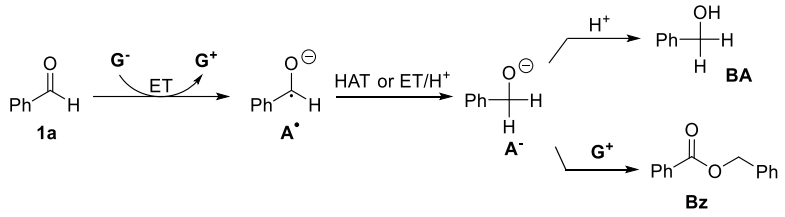
Reaction conditions : **1a** (0.2 mmol), **2a** (0.36 mmol), **3a** (0.2 mmol), **C1·HI** (10 mol%), KO^{t}Bu (0.3 mmol) in solvent (0.6 mL) for 24 h at r.t, Ar. ^{1}H NMR conversion calculated in relation to **3a.** [a] 18 h. [b] 48 h. [c] 60 °C. [d] 0.1 M (2 mL). [e] .0.5 M (0.4 mL). n.o. : not observed

Comparison of bases (entries 1-6): Different nucleophilic bases ($NaNH_2$, NaO^{t}Bu), not soluble in MTBE, were compared to KO^{t}Bu in DMF but were slightly less efficient. An improved stabilization of the SED enolate **G**$^-$ by the potassium cation could explain the better reactivity of KO^{t}Bu compared to NaO^{t}Bu. Non-nucleophilic bases like piperidine or DBU gave no reduction at all.

Time, temperature and concentration optimization: A monitoring of the reaction progress at 18, 24 and 48h showed that 24h was the optimal reaction time to reach 69% (entry 1), as only a few more percents were gained at 48h (76%, entry 8). Increasing the temperature to 60°C did not improve neither the conversion (63%, entry 9). Evaluation of different solvent concentrations (0.1 and 0.5 M) confirmed the optimal quantity at 0.33 M (entries 10-11).

Along the formation of ester **4a**, note that traces of benzyl benzoate **Bz** and benzyl alcohol **BA** could be observed in the reaction mixtures. Both products probably arose from the competitive reduction of benzaldehyde **1a** by the Breslow enolate **G**$^-$ (Scheme 1).[13] In our conditions, the selective reduction of iodoarenes **2** largely prevailed over the reduction of **1a**.

[13] Conversion of **1a** into the cross-coupled ester **Bz**, known as the Tishchenko Reaction, usually operates by metal catalysis: a) T. Seki, T. Nakajo, M. Onaka, *Chem. Lett.*, **2006**, *35*, 824-829. b) The Tishchenko Reaction, A. M. P. Koskinen, A. O. Kataja *in* Organic Reactions, **2015**, *86*, (Ed. S. E. Denmark *et al*, John Wiley & Sons, Inc).



*Scheme 1 – Suggested mechanisms for the formation of benzyl alcohol **BA** and benzyl benzoate **Bz**.*

In the absence of the iodoarene, the aldehyde is totally converted into a mixture of benzil, benzoin, and benzyl alcohol **BA**, mainly. The benzyl benzoate **Bz** and *tert*-butyl benzoate **4a** were seen at trace levels. Such aldehyde reduction underlines the strong electron-donor nature of the imidazolylidene-based Breslow catalyst.

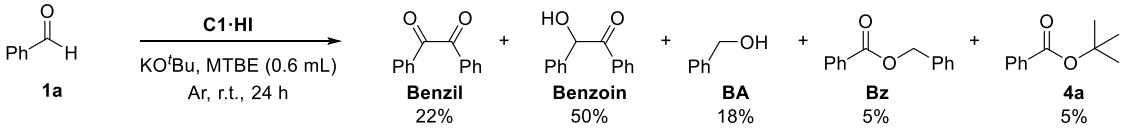
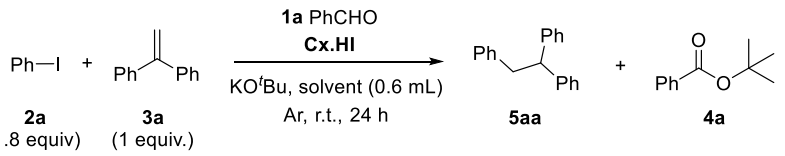


Table S2 - Optimization of the reaction conditions – Part 2



2a (1.8 equiv) **3a** (1 equiv.) **5aa** **4a**

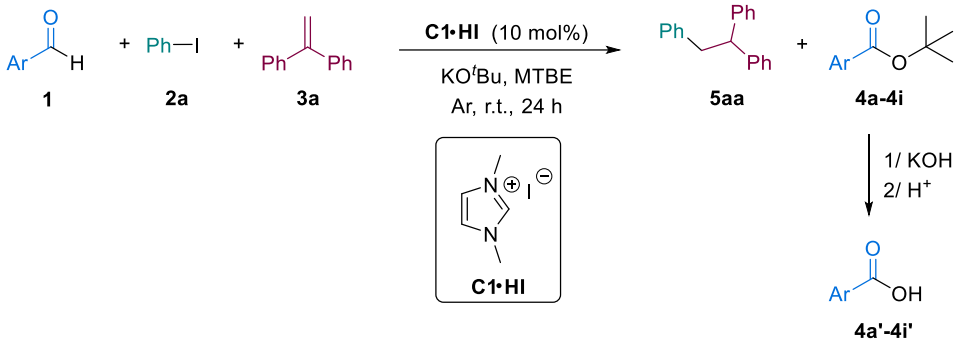
Entry	Cx.HI (loading mol%)	Solvent (BDE_{C-H} kcal/mol)	1a (equiv.)	^{1}H NMR conv. of 5aa (%)	^{1}H NMR conv. of 4a (%)[a]
1	-	MTBE	1	28	16
2	**C1 (10)**	MTBE	1	69	51
3	**C1 (10)**	MTBE (97)[b]	1.5	76 (60)	52
4	**C1 (10)**	MTBE	2	76	53
5	**C1 (10)**	MTBE	1.5[c]	76	63
6	**C1 (5)**	MTBE	1.5	61	52
7	**C1 (15)**	MTBE	1.5	70	49
8	**C1 (20)**	MTBE	1.5	62	46
9	**C1 (10)**	DMF (85-93)	1.5	29	75
10	**C1 (10)**	CH_3CN (96)	1.5	21	30
11	**C1 (10)**	THF (92)	1.5	33	52
12	**C1 (10)**	1,4-dioxane (97)	1.5	51	48
13	**C1 (10)**	Et_2O (93)	1.5	50	59
14	**C1 (10)**	Toluene (89)	1.5	52	54
15	**C1 (10)**	Benzene (113)	1.5	57	53
16	**C1 (10)**	Pentane (100)	1.5	54	59
17	**C4 (10)**	MTBE	1.5	61	65
18	**C3 (10)**	MTBE	1.5	43	59
19	**C2 (10)**	MTBE	1.5	11	68
20	**C5 (10)**	MTBE	1.5	68	49
21	**C6 (10)**	MTBE	1.5	55	40

Reaction conditions : **1a** (1-2 equiv.), **2a** (0.36 mmol), **3a** (0.2 mmol), **Cx.HI** (5-20 mol%), KO^{t}Bu (0.3 mmol) in MTBE (0.6 mL) for 24 h at r.t, Ar. (Yield given in parentheses). [a] ^{1}H NMR conversion relative to the arylation product **5aa**. [b] Corresponding to BDE_{C-H} of ETBE. [c] **2a** (2.5 equiv).

Reagent ratio: Increasing the quantity of benzaldehyde **1a** to 1.5 equivalent improved the conversion of **5aa** to 76% (entry 3). With 2 equivalents of **1a**, proportion of **5aa** was unchanged but a substantial increased proportion of benzyl benzoate **Bz** was noticed (entry 4). Higher quantity of **2a** did not change the outcome (entry 5). Increasing the catalyst loading to 15 or 20 mol% slightly decreased the rate of **5aa** (entries 7-8).

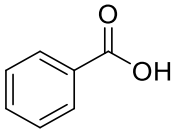
Polar solvents: Polar solvents known to favor electron-transfer reactions, such as dimethylformamide, acetonitrile or THF, were herein less efficient solvents, leading to drastic drops of the conversion in **5aa** (21-33%) (entries 9-11).

b. Synthesis and characterization of carboxylic acids **4'**



To facilitate the purification, all *tert*-butyl benzoate derivatives were hydrolyzed and isolated as the corresponding carboxylic acid.

Procedure B: In a glovebox under argon atmosphere, pre-catalyst **C1•HI** (10 mol%, 0.02 mmol, 4.3 mg) and KO^{t}Bu (1.5 equiv., 0.3 mmol, 32.3 mg) were dissolved in dry methyl *tert*-butyl ether (0.6 mL). The solution was stirred 10 min at r.t. before addition of the aldehyde (1.5 equiv., 0.3 mmol), iodobenzene **2a** (1.8 equiv., 0.35 mmol, 39 µL) and 1,1-diphenylethylene **3a** (1 equiv., 0.2 mmol, 34 µL). The mixture was stirred at r.t. for 24h. The reaction was then quenched with water and the crude was heated at reflux with KOH in EtOH overnight. After hydrolysis, the aqueous phase was extracted with dichloromethane (3 x 5 mL) and then acidified upon dropwise addition of a solution of HCl_{aq} (1 M) until precipitation of a solid. The solid was filtered, washed with water and dried under vacuum. When no precipitation occurred, the acidic aqueous phase was extracted with dichloromethane. The combined organic layers were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum to afford the corresponding pure carboxylic acid.



Benzoic acid, 4a' – [CAS : 854908-61-5] – $C_7H_6O_2$

4a' was synthesized following **procedure B** from benzaldehyde (29 µL) and obtained as a white solid (29 mg, 82%).

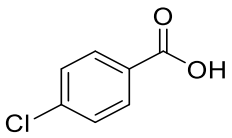
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 8.4, 1.0 Hz, 2H, H^{Ar}), 7.62 (t, J = 7.4 Hz, 1H, H^{Ar}), 7.49 (t, J = 7.7 Hz, 2H, H^{Ar}).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0 (COOH), 134.0 (CH^{Ar}), 130.4 (2 x CH^{Ar}), 129.4 (C^{Ar}), 128.7 (2 x CH^{Ar}).

HRMS (ESI) *m/z* calcd for $C_7H_5O_2^-$: 121.0295, $[M-H]^-$; found: 121.0299.

Spectral data agrees with the reported literature[14].

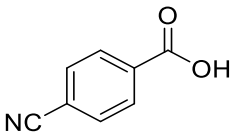
[14] P. Sathyanarayana, O. Ravi, P. Reddy Muktapuram, S. R. Bathula, *Org. Biomol. Chem.*, **2015**, *13*, 9681-9685.



4-Chlorobenzoic acid, 4b' – [CAS : 74-11-3] – $C_7H_5ClO_2$

4b' was synthesized following **procedure B** from 4-chlorobenzaldehyde (41 mg) and obtained as a white solid (32 mg, 70%).

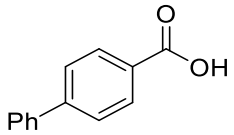
^{1}H NMR (400 MHz, $CDCl_3$): δ 13.16 (s, 1H, COOH), 7.94 (d, *J* = 8.7 Hz, 1H, H^{Ar}), 7.57 (d, *J* = 8.7 Hz, 1H, H^{Ar}).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5 (COOH), 137.8 (C^{Ar}), 131.2 (2 x CH^{Ar}), 129.6 (C^{Ar}), 128.8 (2 x CH^{Ar}).
Spectral data agrees with the reported literature[14].



4-Cyanobenzoic acid, 4c' – [CAS : 619-65-8] – $C_8H_5NO_2$

4c' was synthesized following **procedure B** from 4-cyanobenzaldehyde (37.8 mg) and obtained as a white solid (10 mg, 22%).

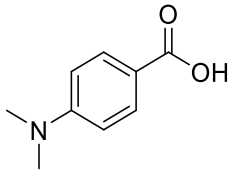
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.3 Hz, 2H, H^{Ar}), 7.98 (d, *J* = 8.3 Hz, 2H, H^{Ar}).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1 (COOH), 132.7 (2 x CH^{Ar}), 129.9 (2 x CH^{Ar}), 118.2 (C^{Ar}), 115.1 (C^{Ar}).
Spectral data agrees with the reported literature[14].



[1,1'-Biphenyl]-4-carboxylic acid, 4d'– [CAS : 92-92-2] – $C_{13}H_{10}O_2$

4d' was synthesized following **procedure B** from [1,1'-biphenyl]-4-carbaldehyde (53 mg) and obtained as a light yellow solid (45 mg, 79%).

^{1}H NMR (400 MHz, DMSO_d_6): δ 12.97 (s, 1H, COOH), 8.03 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 7.80 (d, *J* = 8.5 Hz, 2H, H^{Ar}), 7.73 (d, *J* = 7.0 Hz, 2H, H^{Ar}), 7.52-7.48 (m, 2H, H^{Ar}), 7.44-7.40 (m, 1H, H^{Ar}).
^{13}C NMR (101 MHz, DMSO_d_6): δ 167.2 (COOH), 144.3 (C^{Ar}), 139.0 (C^{Ar}), 130.0 (2 x CH^{Ar}), 129.7 (C^{Ar}), 129.1 (2 x CH^{Ar}), 128.3 (CH^{Ar}), 127.0 (2 x CH^{Ar}) , 126.9 (2 x CH^{Ar}).
Spectral data agrees with the reported literature[15].

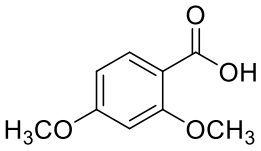


4-(Dimethylamino)benzoic acid, 4e' – [CAS : 619-84-1] – $C_9H_{11}NO_2$

4e' was synthesized following **procedure B** from 4-(dimethylamino)benzaldehyde (43 mg) and obtained as a white solid (33 mg, 70%).

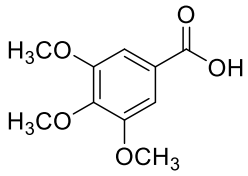
[15] R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, F. Petrucci, A. Prastaro, S. Niembro, A. Shafir, A. Vallribera, *Green Chem.*, **2010**, *12*, 150-158.

^{1}H NMR (400 MHz, DMSO_d_6): δ 12.14 (s, 1 H, COOH), 7.70 (d, J = 12.6 Hz, 2 H, H^{Ar}), 6.60 (d, J = 12.6 Hz, 2 H, H^{Ar}), 2.98 (s, 6 H, 2 x CH_3).
^{13}C NMR (101 MHz, DMSO_d_6): δ 172.1 (COOH), 161.2 (C^{Ar}), 132.4 (C^{Ar}), 120.5 (2 x CH^{Ar}), 111.3 (2 x CH^{Ar}), 41.2 (2 x CH_3).
Spectral data agrees with the reported literature[16] .



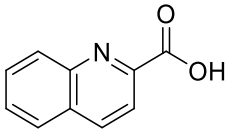
2,4-Dimethoxybenzoic acid, 4f' – [CAS : 91-52-1] – $C_8H_8O_3$
4f' was synthesized following **procedure B** from 2,4-dimethoxybenzaldehyde (48 mg) and obtained as a white solid (26 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.4, 2.0 Hz, 1H, H^{Ar}), 7.60 (d, J = 1.9 Hz, 1H, H^{Ar}), 6.93 (d, J = 8.5 Hz, 1H, H^{Ar}), 3.96 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7 (COOH), 153.9 (C^{Ar}), 148.9 (C^{Ar}), 124.8 (CH^{Ar}), 121.8 (C^{Ar}), 112.5 (CH^{Ar}), 110.5 (CH^{Ar}), 56.2 (OCH_3), 56.2 (OCH_3).
Spectral data agrees with the reported literature[17].



3,4,5-Trimethoxybenzoic acid, 4g' – [CAS : 118-41-2] – $C_{10}H_{12}O_5$
4g' was synthesized following **procedure B** from 3,4,5-trimethoxybenzaldehyde (57 mg) and obtained as a white solid (28 mg, 46%).

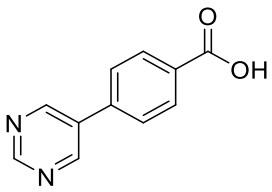
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 2H, 2 x H^{Ar}), 3.93 (s, 3H, OCH_3), 3.93 (s, 6H, 2 x OCH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.59 (COOH) , 153.14 (C^{Ar}), 143.15 (C^{Ar}), 124.21 (C^{Ar}), 107.57 (2 x CH^{Ar}), 61.12 (OCH_3), 56.41 (2 x OCH_3).
Spectral data agrees with the reported literature[17] .



Quinoline-2-carboxylic acid, 4h' – [CAS : 93-10-7] – $C_{10}H_7NO_2$
4h' was synthesized following **procedure B** from quinoline-2-carbaldehyde (45 mg) and obtained as an orange solid (45 mg, 91%).

^{1}H NMR (400 MHz, DMSO_d_6): δ 8.56 (d, J = 8.5 Hz, 1H, H^{Ar}), 8.16 (d, J = 8.0 Hz, 1H, H^{Ar}), 8.11 (d, J = 8.5 Hz, 1H, H^{Ar}), 8.09 (d, J = 8.0 Hz, 1H, H^{Ar}), 7.88 (t, J = 8.0, 7.5 Hz, 1H, H^{Ar}), 7.74 (t, J = 8.0, 7.5 Hz, 1H, H^{Ar}).
^{13}C NMR (101 MHz, DMSO_d_6): δ 166.1 (COOH), 148.5 (C^{Ar}), 146.5 (C^{Ar}), 138.0 (CH^{Ar}), 130.7 (CH^{Ar}), 129.4 (CH^{Ar}), 128.9 (CH^{Ar}), 128.6 (CH^{Ar}), 128.1 (CH^{Ar}), 120.8 (CH^{Ar}).
Spectral data agrees with the reported literature[18].

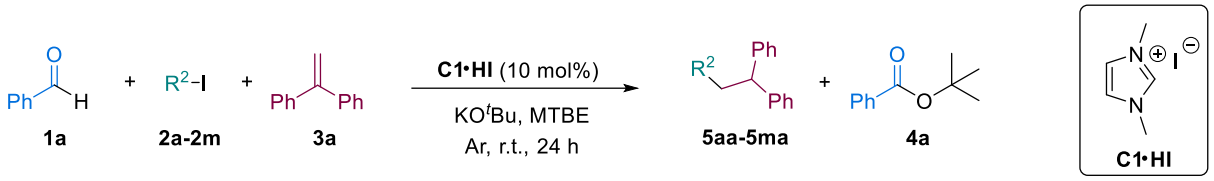
[16] Y-L. Hu, D-J. Li, D-S. Li, *RSC Adv.*, **2015**, *5*, 24936-24943.
[17] A. Nakamura, H. Kanou , J. Tanaka , A. Imamiya , T. Maegawa, Y. Miki, *Org. Biomol. Chem.*, **2018**, *16*, 541-544.
[18] T. D. Tran ,N. B. Pham , Merrick Ekins, J.N. A. Hooper, R. J. Quinn, *Mar. Drugs* **2015**, *13*, 4556-4575.



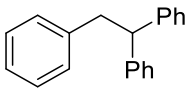
4-(Pyrimidin-5-yl)benzoic acid, 4i' – [CAS : 216959-91-0] – $C_{11}H_8N_2O_2$
4i' was synthesized following **procedure B** from 4-(pyrimidin-5-yl)benzaldehyde (53 mg) and obtained as a light yellow solid (30 mg, 52%).

^{1}H NMR (400 MHz, DMSO_d$_6$): δ 13.13 (s, 1H, COOH), 9.23 (s, 1H, H^{Ar}), 9.20 (s, 2H, H^{Ar}), 8.10-8.04 (m, 2H, H^{Ar}), 7.98-7.91 (m, 2H, H^{Ar}).
^{13}C NMR (101 MHz, DMSO_d$_6$): δ 166.9 (COOH), 157.9 (C^{Ar}), 155.1 (C^{Ar}), 138.0 (C^{Ar}), 132.3 (C^{Ar}), 131.0 (C^{Ar}), 130.1 (C^{Ar}), 127.2 (C^{Ar}).
Spectral data agrees with the reported literature[19].

4. *NHC*-catalyzed arylation of alkenes: scope of iodoaryles



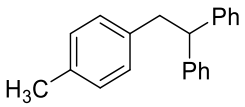
Procedure C: In a glovebox under argon atmosphere, pre-catalyst **C1•HI** (10 mol%, 0.02 mmol, 4.3 mg) and KO^{t}Bu (1.5 equiv., 0.3 mmol, 32.3 mg) were dissolved in dry methyl *tert*-butyl ether (0.6 mL). The solution was stirred 10 min at r.t. before addition of the benzaldehyde **1a** (1.5 equiv., 0.3 mmol, 29 µL), an aryl iodide substrate **2a-2m** (1.8 equiv., 0.35 mmol) and 1,1-diphenylethylene **3a** (1 equiv., 0.2 mmol, 34 µL). The mixture was stirred at r.t. for 24h. The reaction was then quenched with water and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum.



1,1,2-Triphenylethane, 5aa – [CAS : 1520-42-9] – $C_{20}H_{18}$
5aa was synthesized following **procedure C** from iodobenzene **2a** (39 µL) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ dichloromethane 95/5 to 90/10) as a colourless oil (30 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.11 (m, 13H, H^{Ar}), 7.03-6.99 (m, 2H, H^{Ar}), 4.24 (t, *J* = 7.8 Hz, 1H, C*H*), 3.37 (d, *J* = 7.8 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3 (2 x C^{Ar}), 140.1 (C^{Ar}), 128.9 (2 x CH^{Ar}), 128.2 (4 x CH^{Ar}), 127.9 (6 x CH^{Ar}), 126.0 (2 x CH^{Ar}), 125.7 (CH^{Ar}), 52.9 (CH), 41.9 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{20}H_{18}Ag^+$: 365.0454 $[M+Ag]^+$; found: 365.0452.
Spectral data agrees with the reported literature[20].

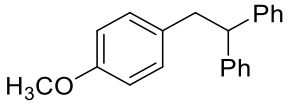
[19] O. Benson, I. da Silva, S. P. Argent, R. Cabot, M. Savage, H. G.W. Godfrey, Y. Yan, S. F. Parker, P. Manuel, M. J. Lennox, T. Mitra, T. L. Easun, W. Lewis, A. J. Blake, E. Besley, S. Yang, M. Schröder, *J. Am. Chem. Soc.*, **2016**, *138*, 45, 14828-14831.
[20] K. Nozawa-Kumada, S. Onuma, K. Ono, T. Kumagai, Y. Iwakawa, K. Sato, M. Shigeno, Y. Kondo, *Chem. Eur. J.*, **2023**, *29*, e202203143.



1-(2,2-Diphenyl-ethyl)-4-methyl-benzene, 5ba – [CAS : 88382-63-2] – $C_{21}H_{20}$

5ba was synthesized following **procedure C** from 4-iodotoluene **2b** (75 mg) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ dichloromethane 95/5 to 90/10) as a white solid (17 mg, 32%).

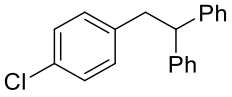
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.2-7.14 (m, 10H, H^{Ar}), 7.00-6.88 (m, 4H, H^{Ar}), 4.23 (t, *J* = 7.8 Hz, 1H, C*H*-CH_2), 3.34 (d, *J* = 7.8 Hz, 2H, CH-C*H*$_2$), 2.27 (s, 3H, C*H*$_3$-Ph).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7 (2 x C^{Ar}), 137.3 (C^{Ar}), 135.4 (C^{Ar}), 129.1 (2 x CH^{Ar}), 128.9 (2 X CH^{Ar}), 128.5 (4 x CH^{Ar}), 128.2 (4 x CH^{Ar}), 126.3 (2 x CH^{Ar}), 53.3 (CH), 41.8 (CH_2), 21.1 (CH_3).
HRMS (ESI-MS) *m/z* calcd for $C_{21}H_{20}Ag^+$: 379.0610 [M+Ag]$^+$; found: 379.0611.
Spectral data agrees with the reported literature[20].



1-(2,2-Diphenyl-ethyl)-4-methoxy-benzene, 5ca – [CAS : 88382-64-3] – $C_{21}H_{20}O$

5ca was synthesized following **procedure C** from 4-iodoanisole **2c** (81 mg) and purified by recrystallization from petroleum ether to afford a white solid (26.5 mg, 46%).

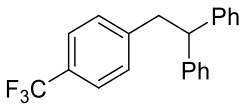
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.18 (m, 8H, H^{Ar}), 7.23-7.12 (m, 2H, H^{Ar}), 6.92 (d, *J* = 8.6 Hz, 2H, H^{Ar}), 6.72 (d, *J* = 8.6 Hz, 2H, H^{Ar}), 4.20 (t, *J* = 7.8 Hz, 1H, CH), 3.75 (s, 3H, OCH_3), 3.32 (d, *J* = 7.8 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9 (C^{Ar}), 144.7 (2 x C^{Ar}), 132.5 (C^{Ar}), 130.1 (2 x CH^{Ar}), 128.5 (4 x CH^{Ar}), 128.2 (4 x CH^{Ar}), 126.3 (2 x CH^{Ar}), 113.6 (2x CH^{Ar}), 55.3 (OCH_3), 53.5 (CH), 41.4 (CH_2).
HRMS (ESI-MS) *m/z* calcd for $C_{21}H_{20}Ag^+$: 395.0560 [M+Ag]$^+$; found: 395.0560.
Spectral data agrees with the reported literature[20].



1-(2,2-Diphenyl-ethyl)-4-chloro-benzene, 5da – [CAS : 88382-66-5] – $C_{20}H_{17}Cl$

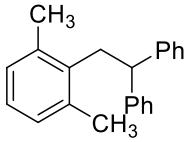
5da was synthesized following **procedure C** from 1-chloro-4-iodobenzene **2d** (82 mg) and obtained after purification by column chromatography on silica gel (cyclohexane/ dichloromethane 95/5) as a white solid (26 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 4H, H^{Ar}), 7.21-7.14 (m, 6H, H^{Ar}), 7.12 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 6.91 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 4.17 (t, *J* = 7.8 Hz, 1H, CH), 3.32 (d, *J* = 7.8 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.2 (2 x C^{Ar}), 138.9 (C^{Ar}), 131.8 (C^{Ar}), 130.5 (2 x CH^{Ar}), 128.6 (4 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 128.1 (4 x CH^{Ar}), 126.5 (2 x CH^{Ar}), 53.2 (CH), 41.6 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{20}H_{17}ClAg^+$ 401.0056 [M+Ag]$^+$; found: 401.0050.
Spectral data agrees with the reported literature[20].



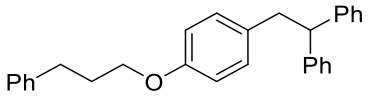
1-(2,2-Diphenyl-ethyl)-4-(trifluoromethyl)-benzene, 5ea – [CAS : 1163695-17-7] – $C_{21}H_{17}F_3$
5ea was synthesized following **procedure C** from 4-Iodobenzotrifluoride **2e** (28 µL) and obtained after purification by column chromatography on silica gel (gradient: petroleum ether/ diethyl ether 95/5 to 90/10) as a white solid (14 mg, 21%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.1 Hz, 2H, H^{Ar}), 7.29-7.15 (m, 10H, H^{Ar}), 7.09 (d, J = 8.0 Hz, 2H, H^{Ar}), 4.22 (t, J = 7.8 Hz, 1H, C*H*-CH_2), 3.42 (d, J = 7.9 Hz, 2H, CH-C*H*$_2$).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5 (C^{Ar}), 144.0 (2 x C^{Ar}), 129.5 (2 x CH^{Ar}), 128.6 (4 x CH^{Ar}), 128.4 (q, J = 32.6 Hz, *C*^{Ar}-CF_3), 128.1 (4 x CH^{Ar}), 126.6 (2 x CH^{Ar}), 125.2 (q, J = 3.9 Hz, 2 x CH^{Ar}), 124.5 (q, J = 272.0 Hz, Ph-*C*F_3), 53.0 (CH), 42.0 (CH_2).
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.28 (s).
HRMS (ESI) *m/z* calcd for $C_{21}H_{17}F_3Ag^+$ 433.0328 $[M+Ag]^+$; found: 433.0323.
Spectral data agrees with the reported literature[20].



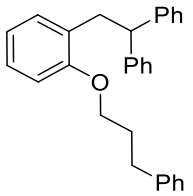
(2-(2,6-Dimethylphenyl)ethane-1,1-diyl)dibenzene, 5fa – $C_{22}H_{22}$
5fa was synthesized following **procedure C** from 1-Iodo-3,5-dimethylbenzene **2f** (50 µL) and obtained after purification by column chromatography on silica gel (gradient: 95/5 cyclohexane/ petroleum ether to 90/10) as beige crystals (18 mg, 32%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.18 (m, 6H, H^{Ar}), 7.15-7.11 (m, 4H, H^{Ar}), 7.01 (m, 1H, H^{Ar}), 6.93 (d, J = 7.4 Hz, 2H, H^{Ar}), 4.12 (t, J = 7.2 Hz, 1H, CH), 3.36 (d, J = 7.2 Hz, 2H, CH_2), 1.93 (s, 6H, 2 x *CH*$_3$-Ph).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9 (2 x C^{Ar}), 137.3 (C^{Ar}), 137.2 (2 x C^{Ar}), 128.4 (4 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 128.2 (2 x CH^{Ar}), 126.4 (2 x CH^{Ar}), 126.0 (CH^{Ar}), 51.4 (CH), 36.2 (CH_2), 20.0 (2 x *CH*$_3$-Ph).
HRMS (ESI) *m/z* calcd for $C_{22}H_{22}Ag^+$: 393.0767 $[M+Ag]^+$; found: 393.0764.



(2-(4-(3-Phenylpropoxy)phenyl)ethane-1,1-diyl)dibenzene, 5ga – $C_{29}H_{28}O$
5ga was synthesized following **procedure C** from 1-Iodo-4-(3-phenylpropoxy)benzene **2g** (117 mg) and obtained after purification by column chromatography on silica gel (eluent: 98/2 cyclohexane/ ethyl acetate) as colorless oil (31 mg, 41%).

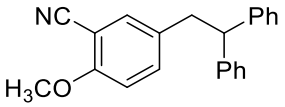
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.11 (m, 15H, H^{Ar}), 6.89 (d, J = 8.6 Hz, 2H, H^{Ar}), 6.70 (d, J = 8.6 Hz, 2H, H^{Ar}), 4.18 (t, J = 7.8 Hz, 1H, *CH*-CH_2), 3.89 (t, J = 6.8 Hz, 2H, CH-*CH*$_2$), 3.30 (d, J = 7.8 Hz, 2H, CH_2), 2.78 (m, 2H, CH_2), 2.11-2.03 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3 (C^{Ar}), 144.7 (2 x C^{Ar}), 141.8 (C^{Ar}), 132.5 (C^{Ar}), 130.1 (2 x CH^{Ar}), 128.7 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.5 (4 x CH^{Ar}), 128.2 (4 x CH^{Ar}), 126.3 (2 x CH^{Ar}), 126.0 (CH^{Ar}), 114.3 (2 x CH^{Ar}), 67.0 (CH), 53.5 (CH_2), 41.4 (CH_2), 32.3 (CH_2), 31.0 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{29}H_{32}NO^+$: 410.2478 $[M+NH_4]^+$; found: 410.2477.



(2-(2-(3-Phenylpropoxy)phenyl)ethane-1,1-diyl)dibenzene, 5ha – $C_{29}H_{28}O$

5ha was synthesized following **procedure C** from 1-Iodo-2-(3-phenylpropoxy)benzene **2h** (117 mg) and obtained after purification by column chromatography on silica gel (gradient: 100 cyclohexane to 95/5 cyclohexane/ dichloromethane) as colorless oil (23 mg, 30%).

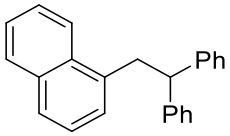
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.11 (m, 15H, H^{Ar}), 7.08 (ddd, *J* = 8.1, 7.4, 1.8 Hz, 1H, H^{Ar}), 6.82 (dd, *J* = 7.4, 1.8 Hz, 1H, H^{Ar}), 6.76 (dd, *J* = 8.1, 1.1 Hz, 1H, H^{Ar}), 6.69 (td, *J* = 7.4, 1.1 Hz, 1H, H^{Ar}), 4.41 (t, *J* = 7.5 Hz, 1H, C*H*-CH_2), 3.94 (t, *J* = 6.1 Hz, 2H, CH_2), 3.39 (d, *J* = 7.5 Hz, 2H, CH-C*H*$_2$), 2.82 (t, *J* = 6.7 Hz, 2H, CH_2), 2.15–2.05 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.1 (C^{Ar}), 145.0 (2 x C^{Ar}), 141.7 (C^{Ar}), 131.0 (2 x C^{Ar}), 128.8 (CH^{Ar}), 128.7 (2 x CH^{Ar}), 128.6 (2 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 127.3 (CH^{Ar}), 126.2 (2 x CH^{Ar}), 126.1 (CH^{Ar}), 120.1 (CH^{Ar}), 111.0 (CH^{Ar}), 66.9 (CH), 51.3 (CH_2), 37.0 (CH_2), 32.6 (CH_2), 31.3 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{29}H_{32}NO^+$: 410.2478 $[M+NH_4]^+$; found: 410.2473.



5-(2,2-Diphenylethyl)-2-methoxybenzonitrile, 5ia – $C_{22}H_{19}NO$

5ia was synthesized following **procedure C** from 5-iodo-2-methoxybenzonitrile **2i** (90 mg) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane 100 to cyclohexane/ ethyl acetate 80/20) as a white solid (25.3 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.22 (m, 4H, H^{Ar}), 7.19 (m, 7H, H^{Ar}), 7.11 (dd, *J* = 8.6, 2.3 Hz, 1H, H^{Ar}), 6.75 (d, *J* = 8.6 Hz, 1H, H^{Ar}), 4.13 (t, *J* = 7.9 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.30 (d, *J* = 7.9 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6 (C^{Ar}), 143.7 (2 x C^{Ar}), 135.0 (CH^{Ar}), 134.0 (CH^{Ar}), 132.9 (C^{Ar}), 128.5 (4 x CH^{Ar}), 127.9 (4 x CH^{Ar}), 126.5 (2 x CH^{Ar}), 116.6 (CN), 111.0 (CH^{Ar}), 101.3 (C^{Ar}), 56.0 (OCH_3), 53.1 (CH), 40.7 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NONa^+$: 336.1359 $[M+Na]^+$; found: 336.1359.

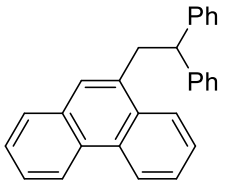


1-(2,2-Diphenylethyl)-naphthalene, 5ja – [CAS : 66375-07-3] – $C_{24}H_{20}$

5ja was synthesized following **procedure C** from 1-iodonaphtalene **2j** (51 µL) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ dichloromethane 95/5 to 90/10) as a yellow solid (29 mg, 49%).

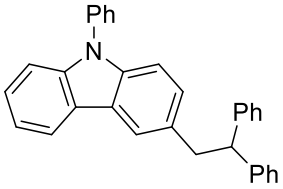
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 1H, H^{Ar}), 7.89-7.85 (m, 1H, H^{Ar}), 7.67 (d, *J* = 8.3 Hz, 1H, H^{Ar}), 7.52-7.47 (m, 2H, H^{Ar}), 7.30-7.16 (m, 11H, H^{Ar}), 6.90 (dd, *J* = 7.1, 1.2 Hz, 1H, H^{Ar}), 4.46 (t, *J* = 7.5 Hz, 1H, C*H*-CH_2), 3.83 (d, *J* = 7.5 Hz, 2H, CH-C*H*$_2$).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8 (2 x C^{Ar}), 136.0 (C^{Ar}), 134.0 (C^{Ar}), 132.1 (C^{Ar}), 129.0 (CH^{Ar}), 128.5 (4 x CH^{Ar}), 128.2 (4 x CH^{Ar}), 127.4 (CH^{Ar}), 126.9 (CH^{Ar}), 126.4 (2 x CH^{Ar}), 126.0 (CH^{Ar}), 125.5 (CH^{Ar}), 125.3 (CH^{Ar}), 123.8 (CH^{Ar}) ,51.8 (CH), 39.4 (CH_2).

HRMS (ESI-MS) *m/z* calcd for $C_{24}H_{20}Ag^+$: 415.0610 $[M+Ag]^+$; found: 415.0608.
Spectral data agrees with the reported literature[20].



9-(2,2-Diphenylethyl)-phenanthrene, 5ka – [CAS : 854908-61-5] – $C_{28}H_{22}$
5ka was synthesized following **procedure C** from 9-iodophenanthrene **2k** (105 mg) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ dichloromethane 95/5 to 90/10) as a yellow solid (28.9 mg, 42%).

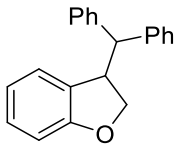
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78-8.70 (m, 1H, H^{Ar}), 8.66-8.61 (m, 1H, H^{Ar}), 8.12 (d, *J* = 7.9 Hz, 1H, H^{Ar}), 7.72-7.55 (m, 4H, H^{Ar}), 7.47 (d, *J* = 1.2 Hz, 1H, H^{Ar}), 7.27-7.22 (m, 8H, H^{Ar}), 7.20-7.14 (m, 3H, H^{Ar}), 4.53 (t, *J* = 7.4 Hz, 1H, CH), 3.85 (d, *J* = 7.4, 0.9 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8 (2 x C^{Ar}), 134.0 (C^{Ar}), 131.7 (C^{Ar}), 131.4 (C^{Ar}), 130.9 (C^{Ar}), 129.7 (C^{Ar}), 128.5 (4 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 128.2 (CH^{Ar}), 128.0 (CH^{Ar}), 126.7 (CH^{Ar}), 126.6 (CH^{Ar}), 126.4 (2 x CH^{Ar}), 126.2 (CH^{Ar}), 126.1 (CH^{Ar}), 124.4 (CH^{Ar}), 123.5 (CH^{Ar}), 122.5 (CH^{Ar}), 51.2(CH), 39.7 (CH_2).
HRMS (ESI-MS) *m/z* calcd for $C_{28}H_{22}Ag^+$: 465.0767 $[M+Ag]^+$; found: 465.0768.
Spectral data agrees with the reported literature[21].



3-(2,2-Diphenylethyl)-9-phenyl-9H-carbazole, 5la – $C_{32}H_{25}N$
5la was synthesized following **procedure C** from 9-iodophenanthrene **2l** (128 mg) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ dichloromethane 95/5 to 90/10) as a white solid (36 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dt, *J* = 7.8, 1.1 Hz, 1H, H^{Ar}), 7.76 (d, *J* = 1.6 Hz, 1H, H^{Ar}), 7.58 - 7.50 (m, 4H, H^{Ar}), 7.44 - 7.38 (m, 1H, H^{Ar}), 7.36 (dd, *J* = 5.9, 1.3 Hz, 2H, H^{Ar}), 7.28-7.22 (m, 9H, H^{Ar}), 7.20 (d, *J* = 8.3 Hz, 1H, H^{Ar}), 7.15 (m, 2H, H^{Ar}), 7.02 (dd, *J* = 8.4, 1.8 Hz, 1H, H^{Ar}), 4.34 (t, *J* = 7.7 Hz, 1H, CH), 3.56 (d, *J* = 7.7 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8 (2 x C^{Ar}), 141.1 (C^{Ar}), 139.6 (C^{Ar}), 138.0 (C^{Ar}), 132.1 (C^{Ar}), 129.9 (2 x CH^{Ar}), 128.5 (4 x CH^{Ar}), 128.3 (4 x CH^{Ar}), 127.4 (CH^{Ar}), 127.4 (CH^{Ar}), 127.1 (2 x CH^{Ar}), 126.3 (2 x CH^{Ar}), 125.9 (CH^{Ar}), 123.4 (C^{Ar}), 123.4 (C^{Ar}), 120.6 (CH^{Ar}), 120.3 (CH^{Ar}), 119.8 (CH^{Ar}), 109.8 (CH^{Ar}), 109.4 (CH^{Ar}), 54.0 (CH), 42.3 (CH_2).
HRMS (ESI) *m/z* calcd for $C_{32}H_{26}N^+$: 424.2060 $[M+H]^+$; found: 424.2057.

[21] F. Bergmann, S. Israelashwili, *J. Am. Chem. Soc.*, **1945**, *67*, 1951-1956.

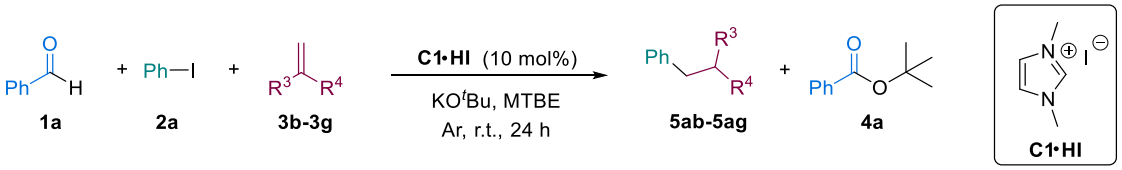


3-(Diphenylmethyl)-2,3-dihydrobenzofuran, 5ma - [CAS : 721395-54-6] – $C_{21}H_{18}O$

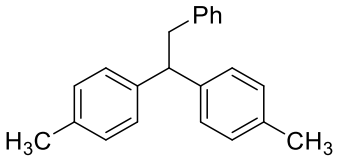
5ma was synthesized following the **procedure C** from (3-(2-iodophenoxy)prop-1-ene-1,1-diyl)dibenzene **2m** (79 mg) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 95/5) as a white solid (17 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.18 (m, 10H, H^{Ar}), 7.12-7.07 (m, 1H, H^{Ar}), 6.79 (dd, J = 8.1, 1.0 Hz, 1H, H^{Ar}), 6.59 (td, J = 7.5, 1.0 Hz, 1H, H^{Ar}), 6.17 (dt, J = 7.5, 1.0 Hz, 1H, H^{Ar}), 4.56 (t, J = 8.9 Hz, 1H, CH_2O), 4.39 (ddd, J = 11.3, 8.9, 5.9 Hz, 1H, CH), 4.23 (dd, J = 9.1, 5.9 Hz, 1H, CH_2O), 4.04 (d, J = 11.3 Hz, 1H, $CHPh_2$).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4 (C^{Ar}), 143.2 (C^{Ar}), 143.1 (C^{Ar}), 129.0 (C^{Ar}), 128.9 (2 x CH^{Ar}), 128.7 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.5 (CH^{Ar}), 128.0 (2 x CH^{Ar}), 126.9 (CH^{Ar}), 126.8 (CH^{Ar}), 125.8 (CH^{Ar}), 119.9 (CH^{Ar}), 109.5 (CH^{Ar}), 75.9 (CH), 56.9 (CH), 46.0 (CH_2O).
Spectral data agrees with the reported literature[22].

5. *NHC*-catalyzed arylation of alkenes: scope of alkenes.

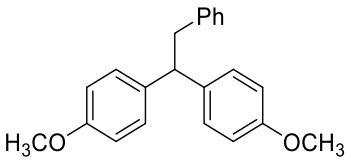


Procedure D: In a glovebox under argon atmosphere, pre-catalyst **C1•HI** (10 mol%, 0.02 mmol, 4.3 mg) and KO^{t}Bu (1.5 equiv., 0.3 mmol, 32.3 mg) were dissolved in dry methyl *tert*-butyl ether (0.6 mL). The solution was stirred 10 min at r.t. before addition of the benzaldehyde **1a** (1.5 equiv., 0.3 mmol, 29 µL), iodobenzene **2a** (1.8 equiv., 0.35 mmol, 39 µL) and an alkene **3b-3g** (1 equiv., 0.2 mmol). The mixture was stirred at r.t. for 24h. The reaction was then quenched with water and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum.



4,4'-(2-Phenylethane-1,1-diyl)bis(methylbenzene), 5ab – [CAS : 144264-33-5] – $C_{22}H_{22}$
5ab was synthesized following **procedure D** from 1,1'-ethenylidenebis[4-methylbenzene] **3b** (42 mg) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 90/10) as a beige oil (25 mg, 46%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-6.99 (m, 13H, H^{Ar}), 4.19 (t, J = 7.8 Hz, 1H, CH), 3.34 (d, J = 7.8 Hz, 2H, CH_2), 2.29 (s, 6H, 2 x CH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ 141.89 (2 x C^{Ar}), 140.68 (C^{Ar}), 135.66 (2 x C^{Ar}), 129.21 (2 x CH^{Ar}), 129.16 (4 x CH^{Ar}), 128.16 (2 x CH^{Ar}), 127.96 (4 x CH^{Ar}), 125.93 (CH^{Ar}), 52.34 (CH), 42.30 (CH_2), 21.11 (2 x CH_3).
Spectral data agrees with the reported literature[20].

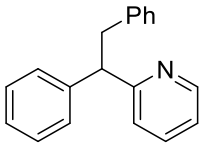
[22] E. Doni, S. Zhou, J. A. Murphy, *Molecules*, **2015**, *20*, 1755-1774.



4,4'-(2-Phenylethane-1,1-diyl)bis(methoxybenzene), 5ac – [CAS : 65921-50-8] – $C_{22}H_{22}O_2$

5ac was synthesized following the **procedure D** from 4,4'-(ethene-1,1-diyl)bis(methoxybenzene) **3c** (48 mg) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ ethyl acetate 90/10) as a yellow oil (21.5 mg, 35%).

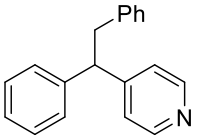
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.12 (m, 3H, H^{Ar}), 7.11-7.08 (m, 4H, H^{Ar}), 7.02-6.98 (m, 2H, H^{Ar}), 6.78 (d, *J* = 8.7 Hz, 4H, H^{Ar}), 4.15 (d, *J* = 7.8 Hz, 1H, CH), 3.75 (s, 6H, 2 x OCH_3), 3.29 (d, *J* = 7.8 Hz, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0 (2 x C^{Ar}), 140.6 (C^{Ar}), 137.2 (2 x C^{Ar}), 129.3 (2 x CH^{Ar}), 129.0 (4 x CH^{Ar}), 128.2 (2 x CH^{Ar}), 125.9 (CH^{Ar}), 113.8 (4 x C^{Ar}), 55.3 (2 x OCH_3), 51.5 (CH), 42.6 (CH_2).
Spectral data agrees with the reported literature[20].



2-(1,2-Diphenylethyl)pyridine, 5ad – [CAS : 5733-74-4] – $C_{19}H_{17}N$

5ad was synthesized following **procedure D** from 2-(1-phenylvinyl)pyridine **3d** (36 mg) and obtained after purification by column chromatography on silica gel (gradient: petroleum ether/ diethyl ether 90/10 to 60/40) as a yellow oil (14.5 mg, 28%).

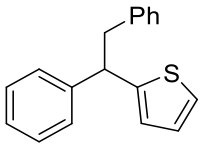
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.9 Hz, 1H, H^{Ar}), 7.59 (td, *J* = 7.7, 1.9 Hz, 1H, H^{Ar}), 7.45-7.41 (m, 2H, H^{Ar}), 7.38-7.32 (m, 2H, H^{Ar}), 7.29-7.22 (m, 3H, H^{Ar}), 7.22-7.13 (m, 5H, H^{Ar}), 4.46 (t, *J* = 7.8 Hz, 1H, CH), 3.76 (dd, *J* = 13.6, 8.0 Hz, 1H, C*H*-H), 3.45 (dd, *J* = 13.7, 7.5 Hz, 1H, CH-*H*).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1 (C^{Ar}), 149.3 (CH^{Ar}), 143.4 (C^{Ar}), 140.5 (C^{Ar}), 136.4 (CH^{Ar}), 129.2 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 128.2 (2 x CH^{Ar}), 126.6 (CH^{Ar}), 125.9 (CH^{Ar}), 123.3 (CH^{Ar}), 121.5 (CH^{Ar}), 55.6 (CH), 41.4 (CH_2).
HRMS (ESI-MS) *m/z* calcd for $C_{19}H_{18}N^+$: 260.1434 $[M+H]^+$; found: 260.1437.
Spectral data agrees with the reported literature[34].



4-(1,2-diphenylethyl)pyridine, 5af – [CAS : 6634-61-3] – $C_{19}H_{17}N$

5af was synthesized following **procedure D** from 4-(1-phenylvinyl)pyridine **3f** (36 mg) and obtained after purification by column chromatography on silica gel (gradient: cyclohexane/ ethyl acetate 90/10 to 70/30) as a colourless oil (25 mg, 50%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48-8.43 (m, 2H, H^{Ar}), 7.29 (t, *J* = 7.1 Hz, 2H, H^{Ar}), 7.24-7.13 (m, 6H, H^{Ar}), 7.10 (d, *J* = 6.0 Hz, 2H, H^{Ar}), 6.99 (d, *J* = 6.6 Hz, 2H, H^{Ar}), 4.21 (t, *J* = 7.9 Hz, 1H, CH), 3.42-3.29 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3 (C^{Ar}), 149.9 (2 x CH^{Ar}), 142.8 (C^{Ar}), 139.4 (C^{Ar}), 129.1 (2 x CH^{Ar}), 128.8 (2 x CH^{Ar}), 128.4 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 128.2 (CH^{Ar}), 127.0 (CH^{Ar}), 126.4 (CH^{Ar}), 123.6 (CH^{Ar}), 52.7 (CH), 41.5 (CH_2).
HRMS (ESI-MS) *m/z* calcd for $C_{19}H_{18}N^+$: 260.1434 $[M + H]^+$; found: 260.1433.

Spectral data agrees with the reported literature[23].



2-(1,2-Diphenylethyl)thiophene, 5ag – [CAS : 2917610-45-6] – $C_{18}H_{16}S$

5ag was synthesized following **procedure D** from 2-(1-phenylethenyl)thiophene **3g** (37 mg) and obtained after purification by column chromatography on silica gel (gradient: petroleum ether/ diethyl ether 100% to 98/2) as a colourless oil (26 mg, 25%).

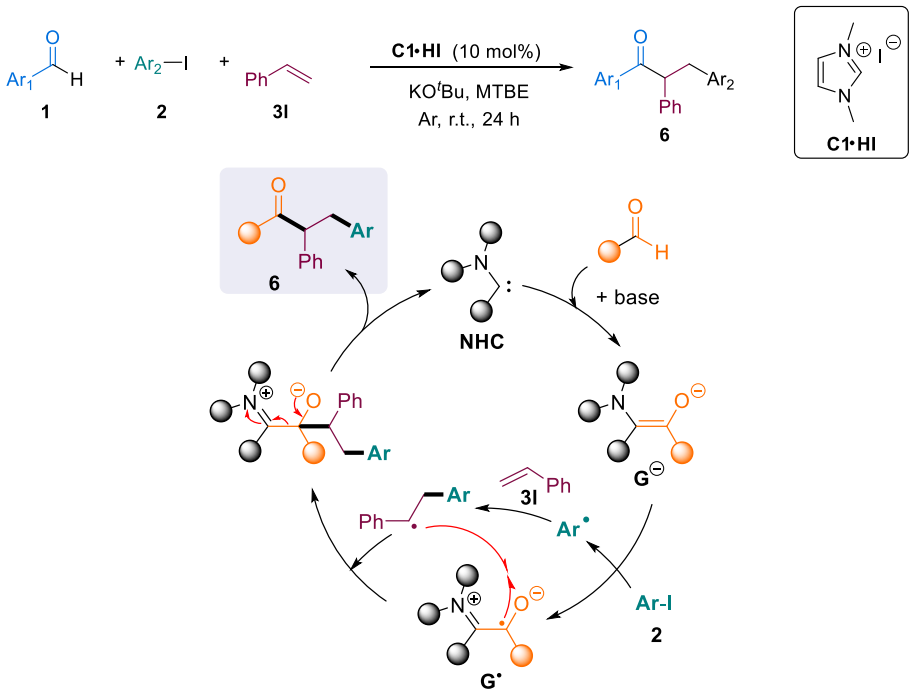
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.08 (m, 9H, H^{Ar}), 7.04-6.99 (m, 2H, H^{Ar}), 6.87 (dd, *J* = 5.1, 3.5 Hz, 1H, H^{Ar}), 6.80-6.77 (m, 1H, H^{Ar}), 4.42 (t, *J* = 7.7 Hz, 1H, CH), 3.43 (dd, *J* = 13.6, 7.2 Hz, 1H, C*H*-H), 3.29 (dd, *J* = 13.6, 8.2 Hz, 1H, CH-*H*).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8 (C^{Ar}), 144.1 (C^{Ar}), 139.8 (C^{Ar}), 129.2 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.2 (2 x CH^{Ar}), 128.0 (2 x CH^{Ar}), 126.8 (CH^{Ar}), 126.6 (CH^{Ar}), 126.2 (CH^{Ar}), 124.3 (CH^{Ar}), 123.8 (CH^{Ar}), 48.9 (CH), 43.9 (CH_2).

HRMS (ESI-MS) *m/z* calcd for $C_{18}H_{17}S^+$: 265.1045 $[M+H]^+$; found: 265.1046.

Spectral data agrees with the reported literature[20].

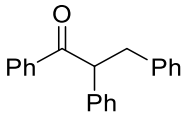
6. *NHC*-catalyzed aryl-acylation of styrene



Procedure E: In a glovebox under argon atmosphere, pre-catalyst **C1•HI** (10 mol%, 0.02 mmol, 4.3 mg) and KO*t*Bu (1.5 equiv., 0.3 mmol, 32.3 mg) were dissolved in dry methyl tert-butyl ether (0.6 mL). The solution was stirred 10 min at r.t. before addition of a benzaldehyde derivative **1** (1 equiv., 0.2 mmol), an aryl iodide substrate **2** (1.8 equiv., 0.35 mmol) and styrene **3l** (1 equiv., 0.2 mmol, 22 µL). The mixture was stirred at r.t. for 24h. The reaction was then quenched with water and the aqueous phase

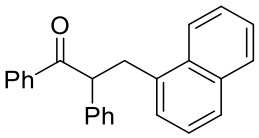
[23] J. J. Eisch, C. A. Kovacs, P. Chobe, Marek P. Boleslawski, *J. Org. Chem.*, **1987**, *52*, 4427-4437.

was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum.



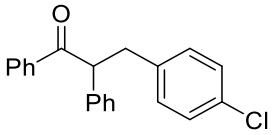
1,2,3-triphenylpropan-1-one, 6aa – [CAS : 4842-45-9] – $C_{21}H_{18}O$
6aa was synthesized following **procedure E** from benzaldehyde **1a** (19.6 µL) and iodobenzene **2a** (38.6 µL) and obtained as a white solid (14 mg, 26%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.4, 1.4 Hz, 2H, H^{Ar}), 7.41-7.34 (m, 1H, H^{Ar}), 7.31-7.25 (m, 2H, H^{Ar}), 7.17-7.05 (m, 8H, H^{Ar}), 7.03-6.98 (m, 2H, H^{Ar}), 4.74 (t, *J* = 7.3 Hz, 1H, CH), 3.49 (dd, *J* = 13.7, 7.5 Hz, 1H, C*H*-H), 2.99 (dd, *J* = 13.7, 7.0 Hz, 1H, CH-*H*).
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4 (CO), 139.9 (C^{Ar}), 139.2 (C^{Ar}), 137.0 (C^{Ar}), 133.1 (CH^{Ar}), 129.3 (2 x CH^{Ar}), 129.1 (2 x CH^{Ar}), 128.8 (2 x CH^{Ar}), 128.6 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.4 (2 x CH^{Ar}), 127.3 (CH^{Ar}), 126.3 (CH^{Ar}), 56.1 (CH_2), 40.3 (CH).
Spectral data agrees with the reported literature[24].



3-(Naphthalen-1-yl)-1,2-diphenylpropan-1-one, 6ja – [CAS : 2252232-59-8] – $C_{25}H_{20}O$
6ja was synthesized following **procedure E** from benzaldehyde **1a** (19.6 µL) and 1-iodonaphtalene **2j** (28 µL) and obtained as a white solid (28.9 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.88-7.81 (m, 3H), 7.69-7.66 (m, 1H), 7.57-7.46 (m, 2H), 7.45-7.39 (m, 1H), 7.34-7.30 (m, 2H), 7.28-7.19 (m, 6H), 7.14-7.08 (m, 1H), 5.01 (t, *J* = 7.0 Hz, 1H), 4.10 (dd, *J* = 14.1, 7.3 Hz, 1H), 3.49 (dd, *J* = 14.2, 6.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4 (CO), 139.6 (C^{Ar}), 136.9 (C^{Ar}), 135.7 (C^{Ar}), 134.0 (C^{Ar}), 133.0 (CH^{Ar}), 132.0 (C^{Ar}), 129.1 (2 x CH^{Ar}), 129.1 (2 x CH^{Ar}), 128.9 (2 x CH^{Ar}), 128.6 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 127.7 (CH^{Ar}), 127.1 (CH^{Ar}), 126.2 (2 x CH^{Ar}), 125.5 (CH^{Ar}), 123.6 (CH^{Ar}), 54.7 (CH_2), 37.1 (CH).
Spectral data agrees with the reported literature[24].

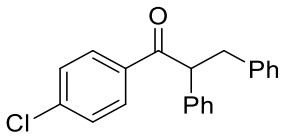


3-(4-Chlorophenyl)-1,2-diphenylpropan-1-one, 6da – [CAS : 35909-57-0] – $C_{21}H_{17}O$
6da was synthesized following **procedure E** from benzaldehyde **1a** (19.6 µL) and 1-chloro-4-iodobenzene **2d** (81.8 mg) and obtained as a white solid (25.2 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 2H, H^{Ar}), 7.48-7.43 (t, *J* = 7.4, 1.2 Hz, 1H, H^{Ar}), 7.35 (t, *J* = 7.6 Hz, 2H, H^{Ar}), 7.27-7.19 (m, 5H, H^{Ar}), 7.15 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 6.99 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 4.75 (t, *J* = 7.3 Hz, 1H, CH), 3.51 (dd, *J* = 13.8, 7.4 Hz, 1H, C*H*-H), 3.03 (dd, *J* = 13.7, 7.1 Hz, 1H, CH-*H*).

[24] L. M. Kabadwal, J. Das, D. Banerjee, *Chem. Commun.*, **2018**, *54*, 14069-14072.

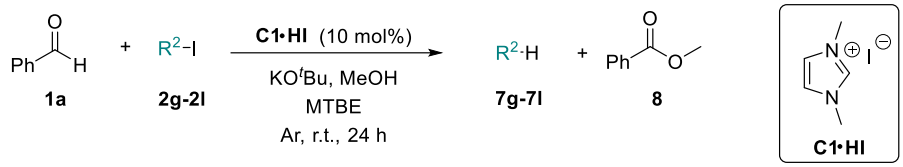
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.1 (CO), 138.9 (C^{Ar}), 138.4 (C^{Ar}), 136.7 (C^{Ar}), 133.1 (CH^{Ar}), 132.1 (C^{Ar}), 130.7 (2 x CH^{Ar}), 129.2 (2 x CH^{Ar}), 128.8 (2 x CH^{Ar}), 128.7 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 128.4 (2 x CH^{Ar}), 127.4 (CH^{Ar}), 56.0 (CH_2), 39.6 (CH).
Spectral data agrees with the reported literature[24].



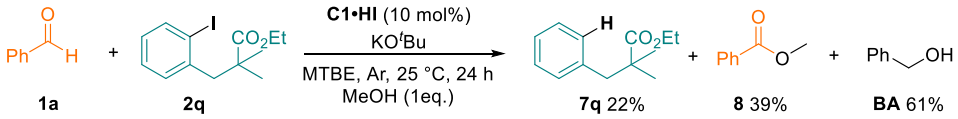
1-(4-Chlorophenyl)-2,3-diphenylpropan-1-one, 6ab – [CAS : 55810-36-1] – $C_{21}H_{17}ClO$
6ab was synthesized following **procedure E** from 4-chlorobenzaldehyde **1b** (27 mg) and iodobenzene **2a** (38.6 µL) and obtained as a white solid (20.3 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.7 Hz, 2H, H^{Ar}), 7.31 (d, *J* = 8.6 Hz, 2H, H^{Ar}), 7.26- 7.11 (m, 8H, H^{Ar}), 7.10-7.05 (m, 2H, H^{Ar}), 4.74 (t, *J* = 7.3 Hz, 1H, CH), 3.55 (dd, *J* = 13.7, 7.5 Hz, 1H, C*H*-H), 3.05 (dd, *J* = 13.7, 7.0 Hz, 1H, CH-*H*).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.2 (CO), 139.7 (C^{Ar}), 139.4 (C^{Ar}), 138.9 (C^{Ar}), 135.1 (C^{Ar}), 130.2 (2 x CH^{Ar}), 129.3 (2 x CH^{Ar}), 129.2 (2 x CH^{Ar}), 128.9 (2 x CH^{Ar}), 128.4 (2 x CH^{Ar}), 128.3 (2 x CH^{Ar}), 127.5 (CH^{Ar}), 126.4 (CH^{Ar}), 56.2 (CH_2), 40.2 (CH).
Spectral data agrees with the reported literature[25].

7. *NHC*-catalyzed reduction of iodoaryles



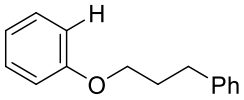
Note on the NHC-catalyzed reduction of iodoaryles: Both oxidative and reductive cycles were concomitant and interdependent, allowing the formation of the two distinct red-ox products in similar ratio. When the SET-reduction of aryl iodides **2g-l** proceeded in good conversion rates (53-87%), **8** was also obtained in good conversions (71-82%). Whereas poor reduction of **2q** into **7q** (22%) led to a smaller quantity of **8** (39%). The rest accounted for the starting aryl iodide **2q** and benzyl alcohol (**BA** 61%). This low reduction rate can be explained by the more negative reduction potential of **2q** (E_p (DMF) = -2.14 V *versus* SCE)[26] and the steric hindrance of the alkyl ester moiety. As a matter of fact, the competitive reduction of the benzaldehyde, leading to the formation of the benzyl alcohol **BA**, prevailed over the reduction of **2q** in this case (**7q** 22% *vs*. **BA** 61 %).



Procedure F: In a glovebox under argon atmosphere, pre-catalyst **C1•HI** (10 mol%, 0.02 mmol, 4.3 mg) and KO^{t}Bu (1.5 equiv., 0.3 mmol, 32.3 mg) were dissolved in dry methyl *tert*-butyl ether (0.6 mL). The solution was stirred 10 min at r.t. before addition of the benzaldehyde **1a** (1 equiv., 0.2 mmol, 20 µL), an iodoaryl substrate **2** (1 equiv., 0.2 mmol) and dry methanol (1 equiv., 0.2 mmol, 8 µL). The mixture

[25] P. J. Barton, ; D. S. Clarke, ; C. D. Davies, ; R. B. Hargreaves, ; J. E. Pease, ; M. T. Rankine, **2004**, WO 2004/011410A1.
[26] J. A. Murphy, S. Zhou, D. W. Thomson, F. Schoenebeck, M. Mahesh, S. R. Park, T. Tuttle, L. E. A. Berlouis, *Angew. Chem. Int. Ed.*, **2007**, *46*, 5178-5183.

was stirred at r.t. for 24 hours. The reaction was then quenched with water and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic phases were then washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated under vacuum. The desired product was purified by silica gel column chromatography.

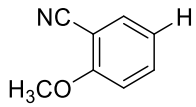


(3-Phenoxypropyl)-benzene - [CAS : 64806-63-9] – $C_{15}H_{16}O$

7g was synthesized following **procedure F** from 1-iodo-4-(3-phenoxypropylbenzene) **2g** (64.9 mg) and obtained after purification by column chromatography on silica gel (eluent cyclohexane/ dichloromethane 95/5) as a yellow oil (24.9 mg, 61%).

7h was synthesized following **procedure F** from 1-iodo-2-(3-phenoxypropylbenzene) **2h** (64.9 mg) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ dichloromethane 95/5) as a yellow oil (22.5 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.23 (m, 7H, H^{Ar}), 7.01-6.91 (m, 3H, H^{Ar}), 3.99 (t, *J* = 6.4 Hz, 2H, O-CH_2), 2.85 (t, *J* = 7.2 Hz, 2H, *Ph*-CH_2), 2.20-2.07 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2 (C^{Ar}-OCH_2), 141.7 (C^{Ar}-CH_2), 129.6 (2 x CH^{Ar}), 128.7 (2 x CH^{Ar}), 128.6 (2 x CH^{Ar}), 126.1 (CH^{Ar}), 120.7 (CH^{Ar}), 114.7 (2 x CH^{Ar}), 66.9 (O-CH_2), 32.3 (CH_2), 31.0 (CH_2).
HRMS (ESI-MS) *m/z* calcd for $C_{15}H_{16}OAg^+$: 319.0247 $[M+Ag]^+$; found: 319.0244.
Spectral data agrees with the reported literature[27].

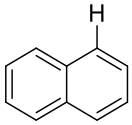


2-Methoxybenzonitrile, 7i – [CAS : 6609-56-9] – C_8H_7ON

Following **procedure F**, the partial reduction of 5-iodo-2-methoxybenzonitrile **2i** (49.7 mg) gave an inseparable mixture (35 mg) of **7i** (66%) and **2i** (34%) after column chromatography on silica gel (eluent: diethyl ether). NMR Yields were calculated from the ratio determined by ^{1}H NMR.

^{1}H NMR of **2i (400 MHz, $CDCl_3$):** δ 7.85- 7.78 (m, 2H, H^{Ar}), 6.75 (d, *J* = 8.7 Hz, 1H, H^{Ar}), 3.92 (s, 3H, OCH_3).
Spectral data agrees with the reported literature[28].

^{1}H NMR of **7i (400 MHz, $CDCl_3$):** δ 7.53-7.57 (m, 2H, H^{Ar}), 6.99-7.00 (m, 2H, H^{Ar}), 3.92 (s, 3H, OCH_3).
Spectral data agrees with the reported literature[27].

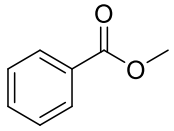


Naphtalene, 7j – [CAS : 91-20-3] – $C_{10}H_8$

7j was synthesized following **procedure F** from 1-iodonaphthalene **2j** (28 µL) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ dichloromethane 99/1) as colorless crystals (13.3 mg, 54%).

[27] J. A. Murphy, J. Garnier, S. R. Park, F. Schoenebeck, S. Zhou, A. T. Turner, *Org. Lett.* **2008**, *10*, 1227-1230.
[28] D. N. Sawant, Y. S. Wagh, P. J. Tambade, K. D. Bhatte, B. M. Bhanage, *Adv. Synth. Catal.* **2011**, *353*, 781-787.

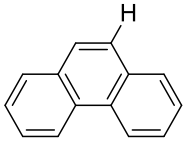
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.53 (m, 4H, H^{Ar}); 7.86-7.90 (m, 4H, H^{Ar}).
^{13}C NMR (101 MHz, $CDCl_3$): δ 133.6 (2 x C^{Ar}), 128.0 (4 x CH^{Ar}), 126.0 (4 x CH^{Ar}).
Spectral data agrees with the reported literature[29].



Methyl benzoate, 8 – [CAS : 93-58-3] – $C_8H_8O_2$

8 was the oxidation product formed following the synthesis of **7j** with **procedure F**. **8** was isolated from the reaction crude after purification by column chromatography on silica gel (eluent: cyclohexane/ dichloromethane 99/1) as a white solid (15.4 mg, 59%).

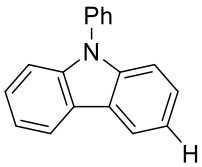
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.5, 1.3 Hz, 2H, H^{Ar}), 7.56 (tt, J = 6.9, 1.4 Hz, 1H, H^{Ar}), 7.44 (t, J = 7.6 Hz, 2H, H^{Ar}), 3.92 (s, 3H, OCH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3 (CO), 133.1 (CH^{Ar}), 130.3 (C^{Ar}), 129.7 (2 x CH^{Ar}), 128.5 (2 x CH^{Ar}), 52.2 (OCH_3).
Spectral data agrees with the reported literature[30].



Phenanthrene, 7k – [CAS : 85-01-8] – $C_{14}H_{10}$

7k was synthesized following **procedure F** from 9-iodophenanthrene **2k** (58.4 mg) and obtained after purification by column chromatography on silica gel (eluent: petroleum ether) as a white solid (21.6 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (dd, J = 7.5, 1.5 Hz, 2H, H^{Ar}), 7.93 (dd, J = 7.5, 1.5 Hz, 2H, H^{Ar}), 7.78 (s, 2H, H^{Ar}), 7.66 (m, 4H, H^{Ar}).
^{13}C NMR (101 MHz, $CDCl_3$): δ 132.2 (2 x C^{Ar}), 130.5 (2 x C^{Ar}), 128.7 (2 x CH^{Ar}), 127.1 (2 x CH^{Ar}), 126.7 (4 x CH^{Ar}), 122.8 (2 x CH^{Ar}).
HRMS (ESI-MS) *m/z* calcd for $C_{14}H_{10}Ag^+$: 284.9828 $[M+Ag]^+$; found: 284.9830.
Spectral data agrees with the reported literature[29].



9-Phenyl-9*H*-carbazole, 7l – [CAS : 1150-62-5] – $C_{18}H_{13}N$

7l was synthesized following **procedure F** from 3-iodo-9-phenyl-9*H*-carbazole **2l** (70.9 mg) and obtained after purification by column chromatography on silica gel (eluent: cyclohexane/ dichloromethane 99/1) as a white solid (21 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 7.7 Hz, 2H, H^{Ar}), 7.64-7.55 (m, 4H, H^{Ar}), 7.47 (m, 1H, H^{Ar}), 7.41 (d, J = 3.5 Hz, 4H, H^{Ar}), 7.32-7.27 (m, 2H, H^{Ar}).

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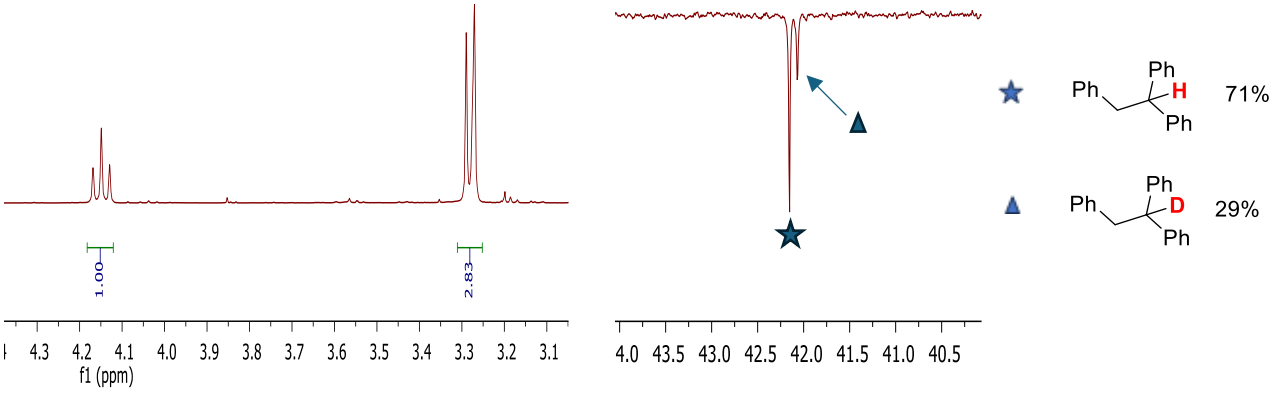
[29] J.A. Murphy, S. Zhou, D.W. Thomson, F. Schoenebeck, M. Mahesh, S.R. Park, T. Tuttle, L.E.A. Berlouis, *Angew. Chem. Int. Ed.* **2007**, *46*, 5178-5183.
[30] M. Majek, A. J. von Wangelin*, Angew. Chem. Int. Ed*. **2015**, *54*, 2270 -2274.

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.0 (2 x C^{Ar}), 137.9 (C^{Ar}), 130.0 (2 x CH^{Ar}), 127.6 (CH^{Ar}), 127.3 (2 x CH^{Ar}), 126.1 (2 x CH^{Ar}), 123.5 (2 x CH^{Ar}), 120.4 (2 x CH^{Ar}), 120.0 (2 x CH^{Ar}), 109.9 (2 x CH^{Ar}).
HRMS (ESI-MS) *m/z* calcd for $C_{18}H_{13}NAg^+$: 350.0093 $[M+Ag]^+$; found: 350.0089.
Spectral data agrees with the reported literature[31].

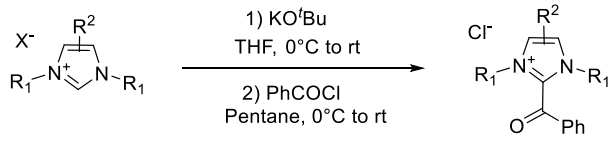
8. Mechanistic studies

a. NMR spectra of isotopic labelling experiments

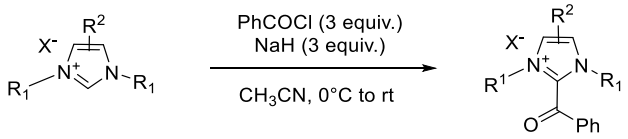
^{1}H and ^{13}C APT NMR of the reaction crude with 1a and CD_3OD (in $CDCl_3$, zoom on 3.1-4.3 ppm and 40-44 ppm area, respectively)



b. Synthesis of acylium salts **G$^+$**



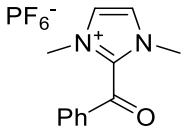
Procedure G: To a solution of potassium tert-butoxide KO^{t}Bu (1.2 equiv.) in dry THF (10 mL) at 0°C under argon atmosphere was added dropwise *via* cannula a suspension of the corresponding carbene precursor salt (1 equiv.) in dry THF (10 mL). The addition was performed under vigorous stirring. After warming to room temperature, volatiles were removed under vacuum on a Schlenk line. The crude was extracted with dry pentane, filtered *via* cannula and benzoyl chloride (1.2 equiv.) was added at 0 °C to the filtrate (instantaneous precipitation was observed). After stirring at room temperature for 15 minutes, the solid was filtered *via* cannula and washed with dry diethyl ether several times. Recrystallization from dry dichloromethane/diethyl ether mixture led to pale yellow to colourless crystals.



Procedure H: In a Schlenk tube under argon atmosphere, a solution of corresponding carbene precursor salt (1 equiv.) and benzoyl chloride (3 equiv.) in dry acetonitrile (20 mL) was cooled to 0 °C.

[31] Y. Zhou, J.G. Verkade, *Adv. Synth. Catal.* **2010**, *352*, 616-620.

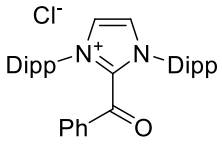
Sodium hydride (NaH) (60% wt. in oil; 3 equiv.) was added to this mixture portion-wise over 1.5 hours. After completion of the reaction (3 hours), volatiles were removed under vacuum on a Schlenk line. *Note that at this stage, an aqueous work-up of a $CDCl_3$ NMR sample is helpful for assessing the stability of the acyl azolium salt towards hydrolysis. Most of salts are stable (if not several wash with dry Et_2O were done following a crystallization by diffusion of diethyl ether into a saturated solution of the salt in acetonitrile.* Cold water (with ice) was added, and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$ and concentrated under vacuum*. Note that when the final counter-anion is hexafluorophosphate, an additional wash with a saturated solution of KPF_6 in water was carried out*. The resulting crude was then triturated in diethyl ether until precipitation was observed, washed with diethyl ether several times and dried under vacuum. Recrystallization from dry dichloromethane/diethyl ether mixture led to pale yellow to colourless crystals.



2-Benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium hexafluorophosphate(V), $G1^+$ – [CAS: 99803-02-8] – $C_{12}H_{13}F_6N_2OP$

Synthetized following **procedure H** from 1,3-dimethylimidazolium hexafluorophosphate (0.83 mmol, 200 mg) and obtained as a brown powder (30 mg, 10 %).

^{1}H NMR (500 MHz, CD_3CN): δ 7.89-7.87 (m, 3H, H^{Ar}), 7.69-7.66 (m, 2H, H^{Ar}), 7.54 (s, 2H, H^{Ar}), 3.75 (s, 6H, 2 x CH_3).
^{13}C NMR (126 MHz, CD_3CN): δ 181.5 (CO), 137.5 (CH^{Ar}), 135.7 (C^{Ar}), 131.1 (2 x CH^{Ar}), 130.7 (2 x CH^{Ar}), 126.1 (3 x CH^{Ar}), 38.1 (2 x CH_3).
^{19}F NMR (376 MHz, CD_3CN): δ -73.00 (d, *JF-P* = 706 Hz).
HRMS (ESI) *m/z* calcd for $C_{12}H_{13}ON_2^+$: 201.1022 $[M]^+$; found: 201.1016.
m. p.: 181 °C.

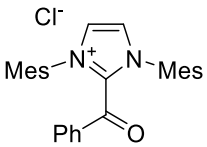


2-Benzoyl-1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium chloride, $G2^+$ – [CAS : 1228185-08-7] – $C_{34}H_{41}ClN_2O$

Synthetized following **procedure G** from 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.44 mmol, 211 mg) and obtained as a white powder (121 mg, 52 %).

^{1}H NMR (500 MHz, CD_3CN): δ 8.89 (s, 2H, H^{Ar}), 7.59 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 7.49 (d, *J* = 7.3 Hz, 2H, H^{Ar}), 7.44 (t, *J* = 7.8 Hz, 2H, H^{Ar}), 7.36 (t, *J* = 7.8 Hz, 2H, H^{Ar}), 7.21 (d, *J* = 7.8 Hz, 4H, H^{Ar}), 2.54 (sept, *J* = 6.8 Hz, 4H, 4 X CH), 1.29 (d, *J* = 6.8 Hz, 12H, 4 x CH_3), 1.20 (d, *J* = 6.7 Hz, 12H, 4 x CH_3).
^{13}C NMR (126 MHz, CD_3CN): δ 179.4 (CO), 145.3 (3 x CH^{Ar}), 140.9 (C^{Ar}), 136.6 (2 x C^{Ar}), 133.6 (C^{Ar}), 132.5 (2 x CH^{Ar}), 129.8 (2 x CH^{Ar}), 129.2 (2 x CH^{Ar}), 128.7 (C^{Ar}) 125.1 (4 x CH^{Ar}), 29.7 (4 x CH), 26.5 (4 x CH_3), 22.6 (4 x CH_3).

Spectral data agrees with the reported literature[32].

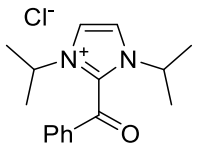


2-Benzoyl-1,3-dimesityl-1H-imidazol-3-ium, $G3^+$ – $C_{28}H_{29}ClN_2O$

Synthetized following **procedure G** from 1,3-dimesityl-imidazolium chloride (0.55 mmol, 188 mg) and obtained as a white powder (150 mg, 62 %).

[32] C. L. Deardorff, R. E. Sikma, C. P. Rhodes, T. W. Hudnall, *Chem. Commun.*, **2016**, *52*, 9024-9027.

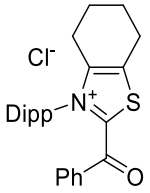
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (s, 2H, H^{Ar}), 7.55 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 7.46 (d, *J* = 7.2 Hz, 2H, H^{Ar}), 7.33 (t, *J* = 7.9 Hz, 2H, H^{Ar}), 6.87 (s, 4H, H^{Ar}), 2.21 (s, 6H, 2 x CH_3), 2.15 (s, 12H, 4 x CH_3).
^{13}C NMR (126 MHz, $CDCl_3$): δ 179.6 (CO), 141.7 (3 C^{Ar}), 139.9 (C^{Ar}), 136.4 (3 x C^{Ar}), 133.8 (2 CH^{Ar}), 133.2 (C^{Ar}), 130.0 (3 CH^{Ar}), 129.6 (2 C^{Ar}), 129.0 (2 CH^{Ar}), 128.6 (2 CH^{Ar}), 128.3 (2 CH^{Ar}), 20.9 (2 x CH_3), 17.9 (4 x CH_3).
HRMS (ESI) m/z calcd for $C_{28}H_{29}ON_2$: 409.2274 $[M\text{-}Cl]^+$; found: 409.2270.
m. p.: 210 °C.



2-Benzoyl-1,3-diisopropyl-1H-imidazol-3-ium, G4$^+$ – $C_{16}H_{21}ClN_2O$

Synthetized following **procedure G** from 1,3-diisopropylimidazolium chloride (1.2 mmol, 300 mg) and obtained as a white powder (76 mg, 22 %)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 2H, H^{Ar}), 7.90 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 7.83 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 7.66 (t, *J* = 7.9 Hz, 2H, H^{Ar}), 4.36 (hept, *J* = 6.7 Hz, 2H, 2 x CH), 1.58 (d, *J* = 6.7 Hz, 12H, 4 x CH_3).
^{13}C NMR (126 MHz, $CDCl_3$): δ 181.9 (CO), 137.7 (CH^{Ar}), 137.2 (C^{Ar}), 134.4 (C^{Ar}), 130.4 (2 x CH^{Ar}), 130.3 (2 x CH^{Ar}), 122.7 (2 x CH^{Ar}), 53.6 (2 x CH), 23.1 (4 x CH_3).
HRMS (ESI) m/z calcd for $C_{16}H_{21}ON_2$: 257.1648 $[M\text{-}Cl]^+$; found: 257.1643.
m. p.: 185 °C.



2-Benzoyl-3-(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-benzothiazolium chloride, G7$^+$ – [CAS : 2761154-39-4] – $C_{26}H_{30}ClNOS$

Synthetized following **procedure G** from 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (1 mmol, 400 mg) and obtained as orange crystalline blocks (34 mg, 18 %).

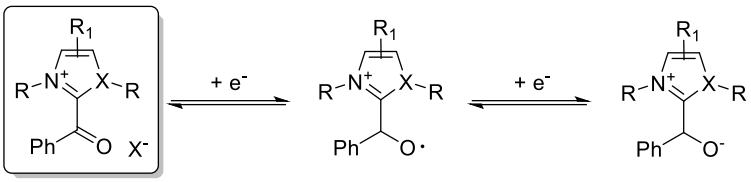
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 7.73 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 7.62-7.55 (m, 3H, H^{Ar}), 7.35 (d, *J* = 7.8 Hz, 2H, H^{Ar}), 3.62 (t, *J* = 6.2 Hz, 2H, CH_2), 2.36 (t, *J* = 6.2 Hz, 2H, CH_2), 2.23 (sept, *J* = 6.8 Hz, 2H, 2 x CH), 2.08-2.02 (m, 2H, CH_2), 1.96-1.89 (m, 2H, CH_2), 1.19 (d, *J* = 6.8 Hz, 6H, 2 x CH_3), 1.08 (d, *J* = 6.8 Hz, 6H, 2 x CH_3).
^{13}C NMR (126 MHz, $CDCl_3$): δ 180.0 (CO), 156.9 (C^{Ar}), 147.6 (C^{Ar}), 144.5 (2 x C^{Ar}), 142.4 (C^{Ar}), 136.3 (CH^{Ar}), 135.2 (C^{Ar}), 132.2 (CH^{Ar}), 131.1 (CH^{Ar}), 131.0 (2 x CH^{Ar}), 129.8 (2 x CH^{Ar}), 125.5 (2 x CH^{Ar}), 29.1 (4 x CH), 26.0 (CH_2), 24.7 (CH_2), 24.3 (2 x CH_3), 22.2 (CH_2), 21.0 (CH_2).
Spectral data agrees with the reported literature.[33]

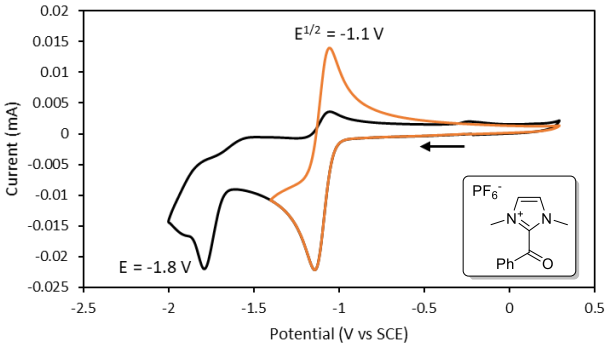
c. Electrochemical characterization of acylium salts **G$^+$**

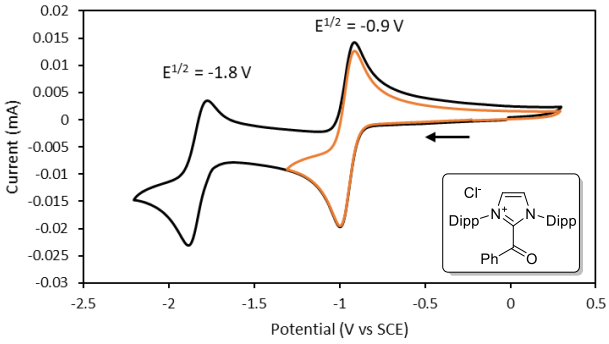
Electrochemical experiments were carried out in a glovebox under an atmosphere of dry argon at 22 °C (air-conditioned room) employing PalmSens4 potentiostat. A silver reference electrode (0.01 M $AgNO_3$ in 0.1 M [^{n}Bu$_4$N]PF_6 in acetonitrile) was used. Cyclic voltammetry experiments were performed in acetonitrile with 0.1 M [^{n}Bu$_4$N]PF_6 electrolyte at 100 mVs^{-1} rate of 1 mM solution of acyl azolium. A vitreous carbon disk (3 mm in diameter) as working electrode and a platinum wire as auxiliary

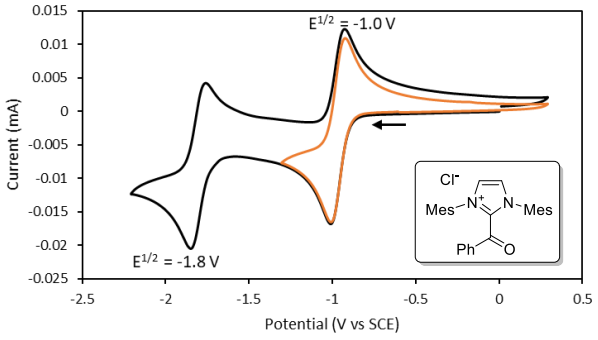
[33] L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil, D. Martin, *Angew. Chem. Int. Ed.*, **2021**, *60*, 26783-26789.

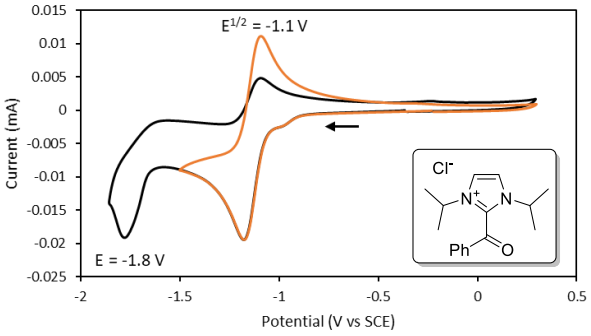
electrode were employed. All potentials are reported in V *vs* SCE. The $E_{1/2}$ of the Fc/Fc^{+} redox couple used as a standard is 0.38 V *vs* SCE in acetonitrile under our conditions.[34]

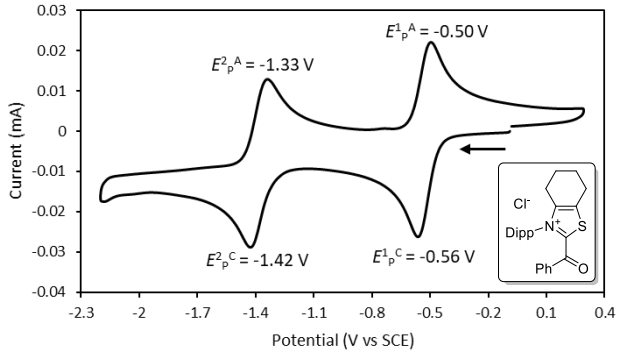








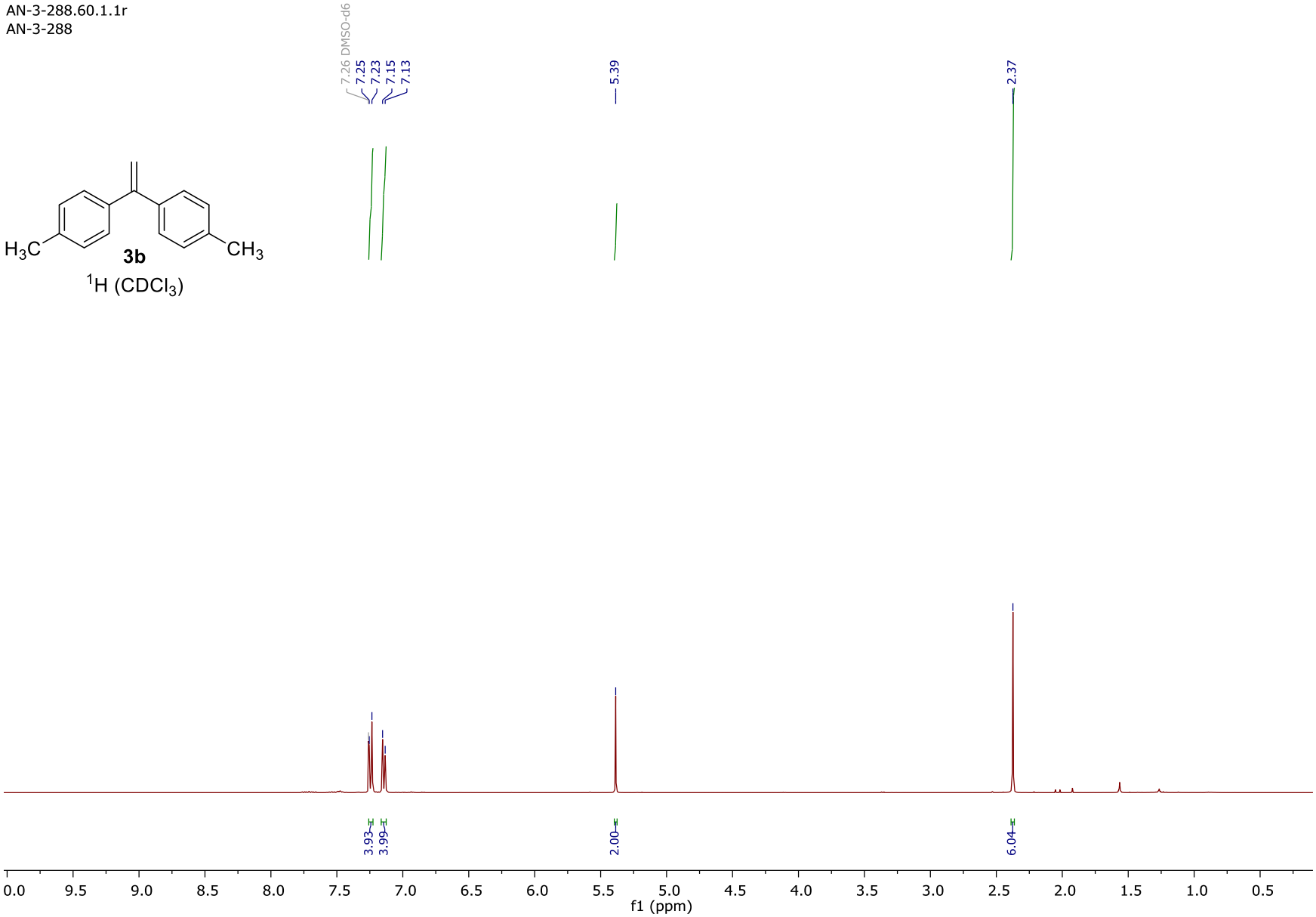




9. NMR spectra

[34] Y. Wang, X. Li, F. Leng, H. Zhu, J. Li, D. Zou, Y. Wu, Y. Wu, *Adv. Synth. Catal.*, **2014**, *356*, 3307-3313.

AN-3-288.60.1.1r
AN-3-288



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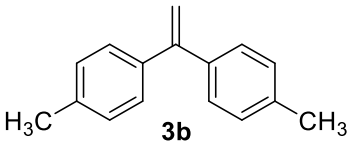
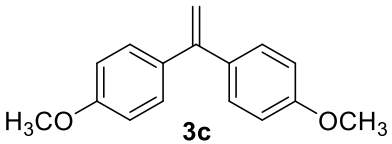
AN-3-288



3b

^{13}C ($CDCl_3$)

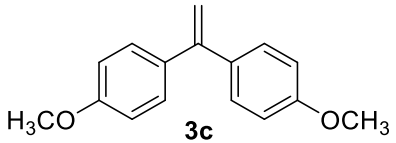
AN-DL023.50.1.1r



3c

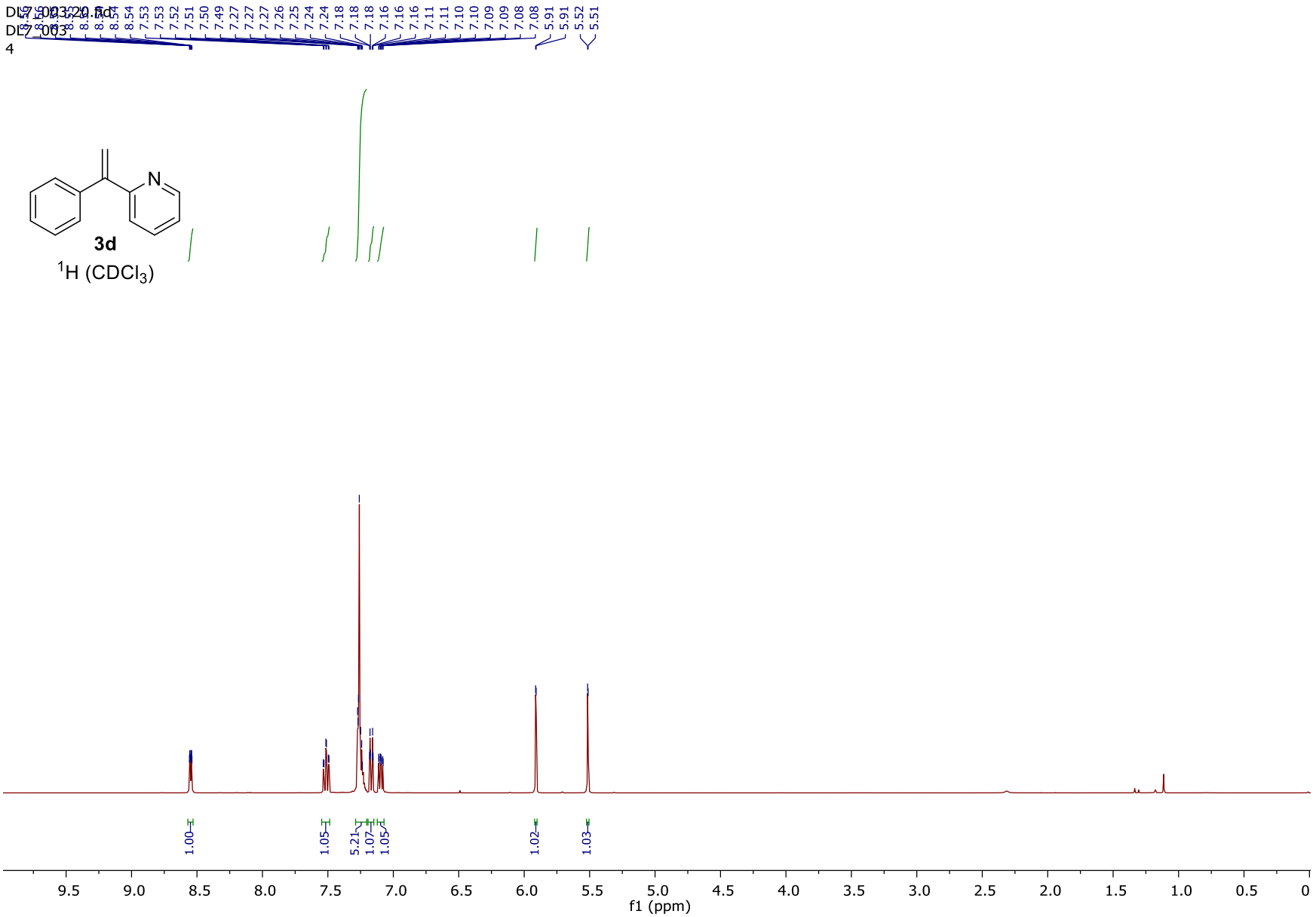
^1H ($CDCl_3$)

AN-DL023.51.1.1r



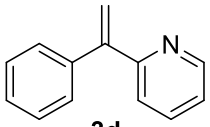
3c

^{13}C ($CDCl_3$)


DL7_003_29.fid
DL7_003
4
8.54
7.53
7.52
7.51
7.50
7.49
7.27
7.26
7.25
7.24
7.18
7.16
7.11
7.10
7.09
7.08
5.91
5.52
5.51
N
3d
^{1}H ($CDCl_3$)
1.00
1.05
5.21
1.07
1.05
1.02
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

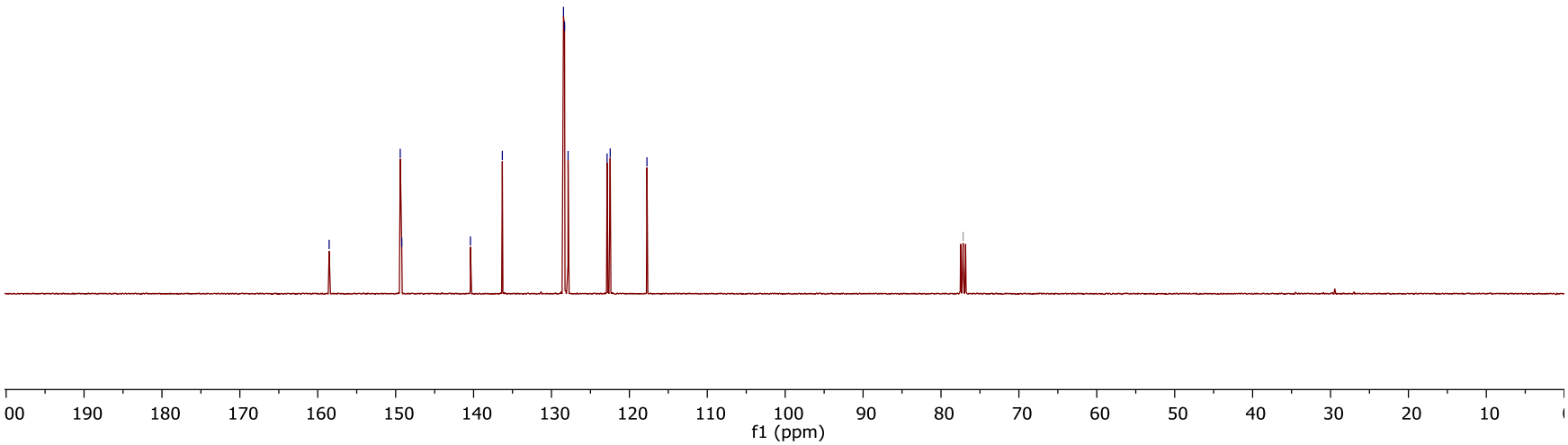
DL7_003.21.fid
DL7_003
4

158.54
149.41
149.22
140.40
136.31
128.46
128.32
127.87
122.86
122.46
117.75
77.16 CDCl3

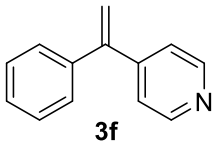


3d

^{13}C ($CDCl_3$)



DL7_002.40.fid
DL7_002
final

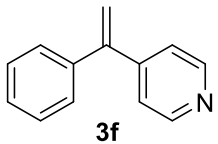


3f

^1H ($CDCl_3$)

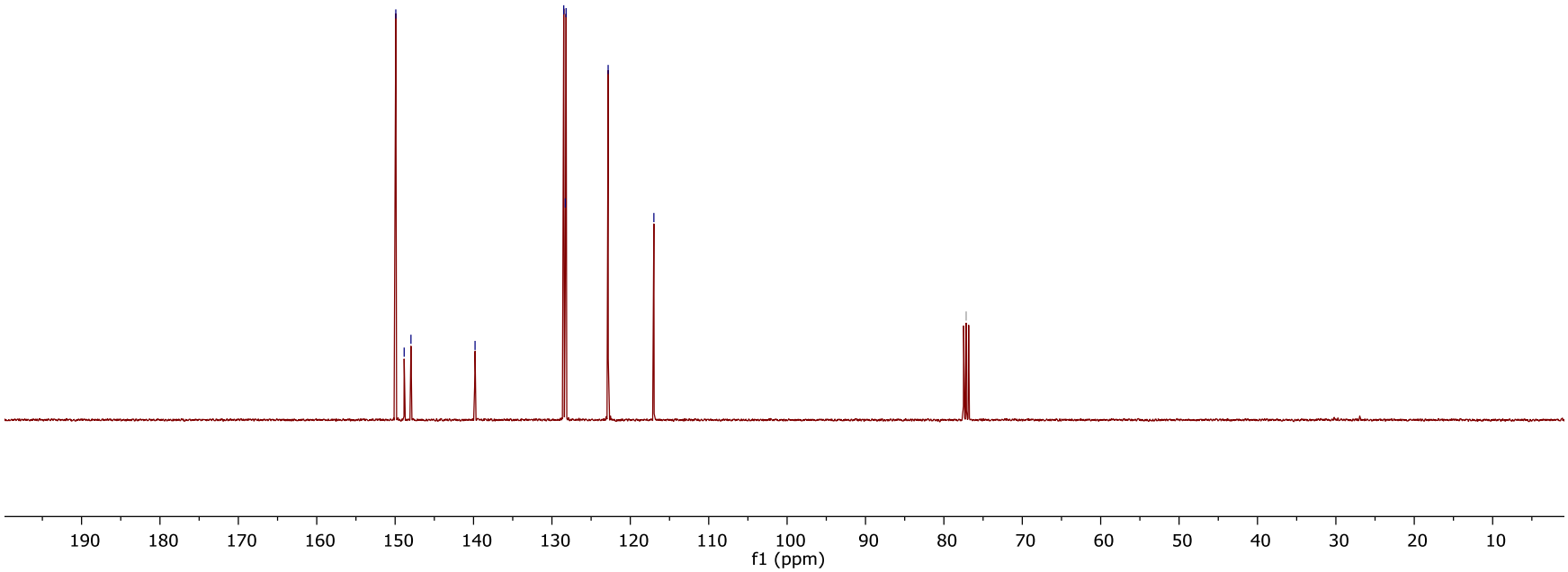
DL7_002.41.fid
DL7_002
final

149.92
148.85
147.98
139.81
128.49
128.29
128.19
122.83
117.00
77.16 CDCl3



3f

^{13}C ($CDCl_3$)



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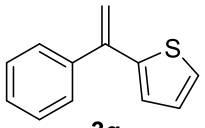
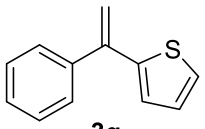
DL7_005
final



3g

^1H ($CDCl_3$)

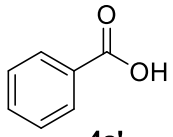
DL7_005.11.fid
DL7_005
final



3g

^{13}C ($CDCl_3$)

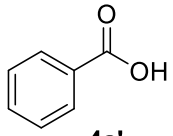
AN-3-210A.22.1.1r
AN-3-210A



4a'

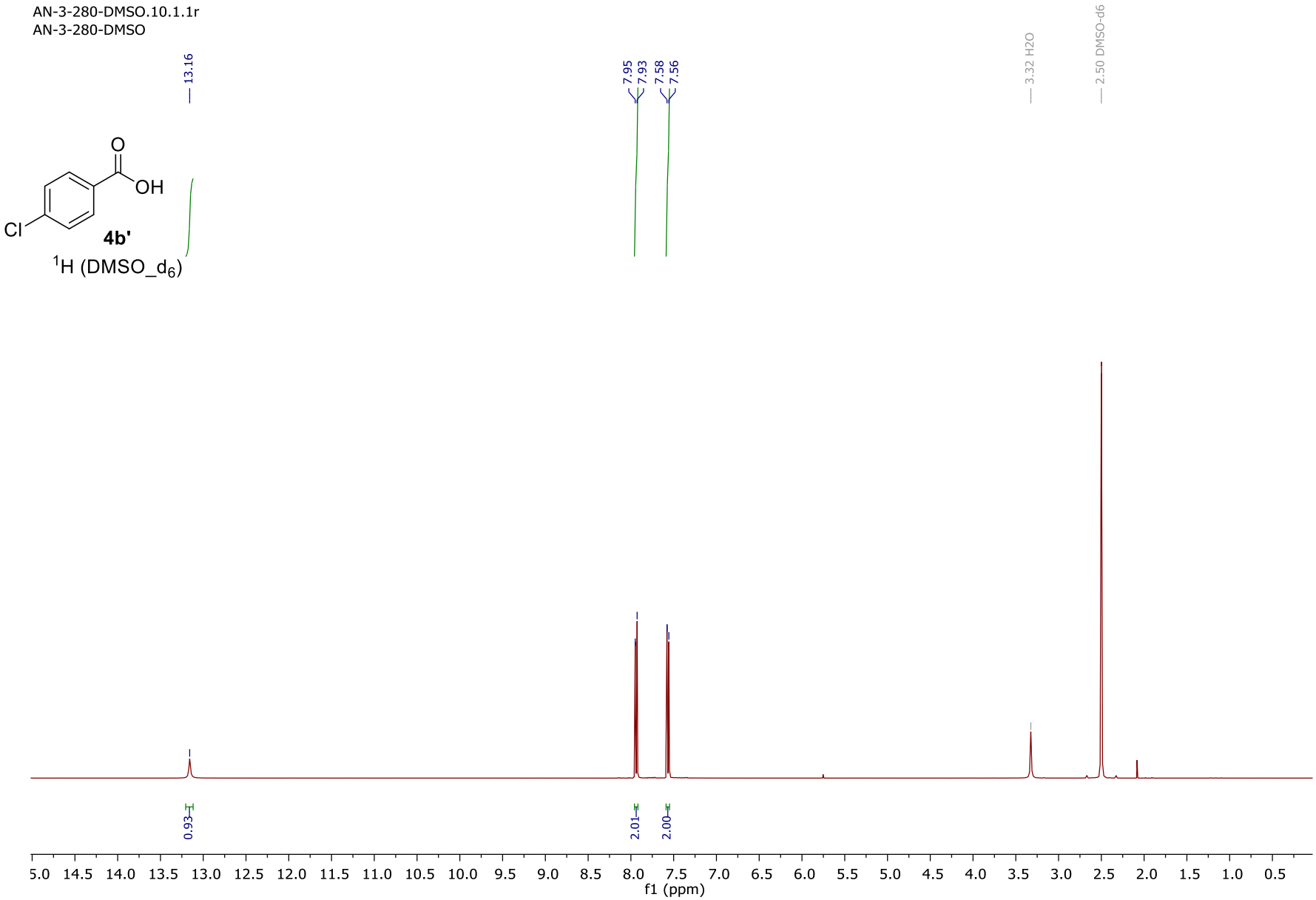
^1H ($CDCl_3$)

AN-3-210A.24.1.1r
AN-3-210A

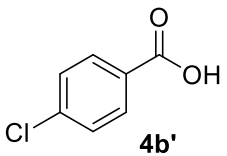


4a'

^{13}C ($CDCl_3$)

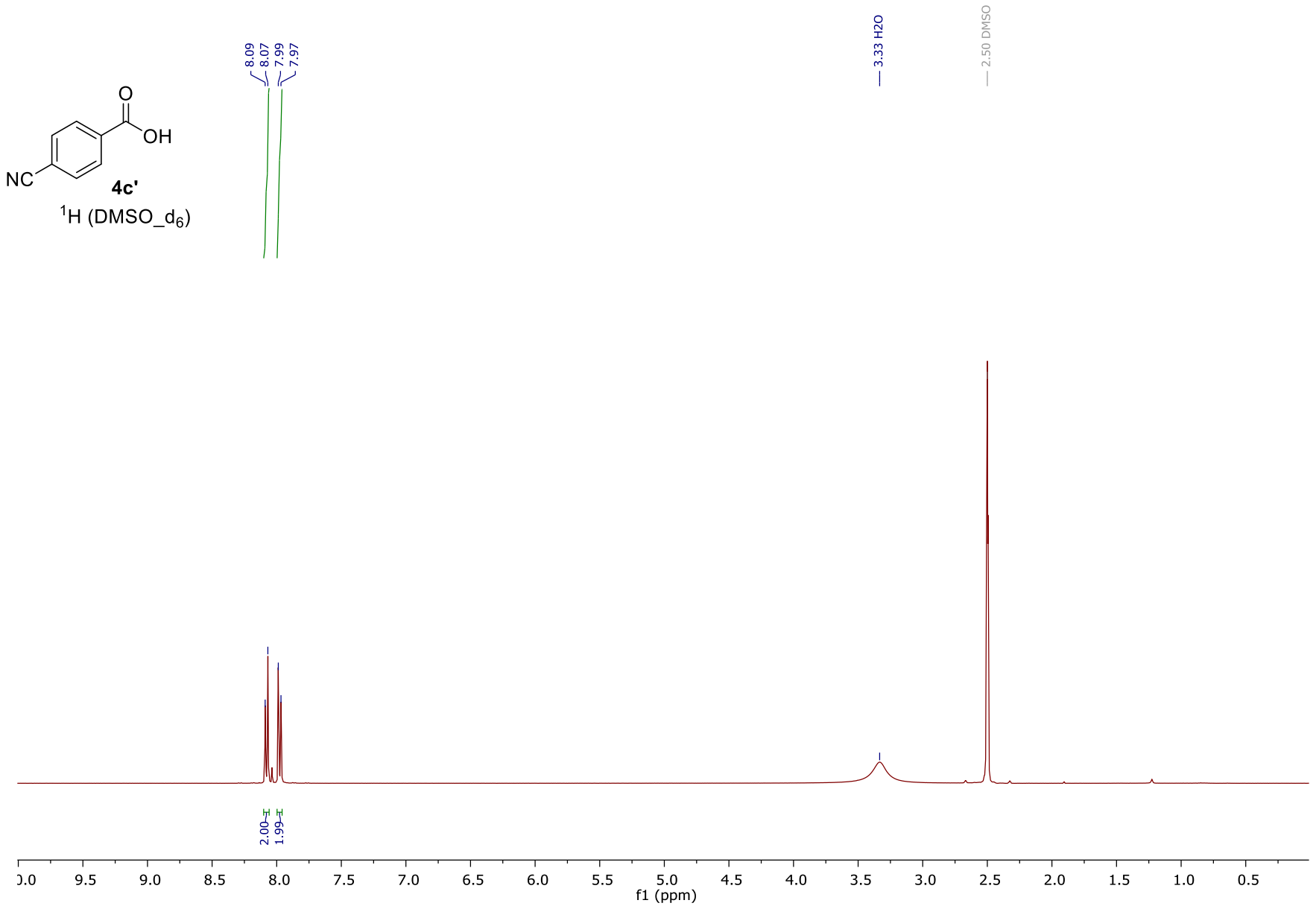

AN-3-280-DMSO.10.1.1r
AN-3-280-DMSO
13.16
7.95
7.93
7.58
7.56
3.32 H2O
2.50 DMSO-d6
O
OH
Cl
4b'
1H (DMSO_d6)
0.93
2.01
2.00
f1 (ppm)

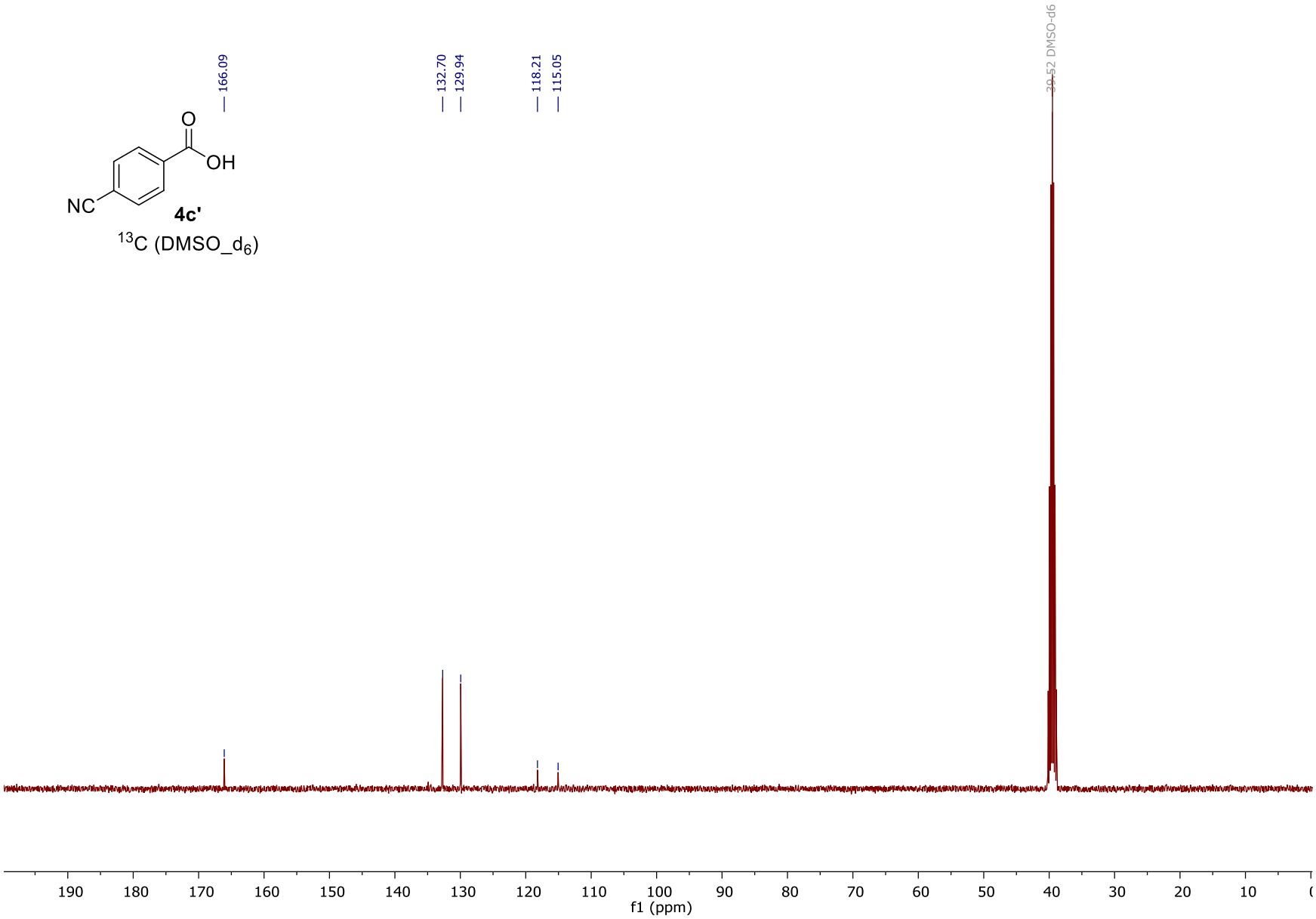
AN-3-280-DMSO.20.1.1r
AN-3-280-DMSO



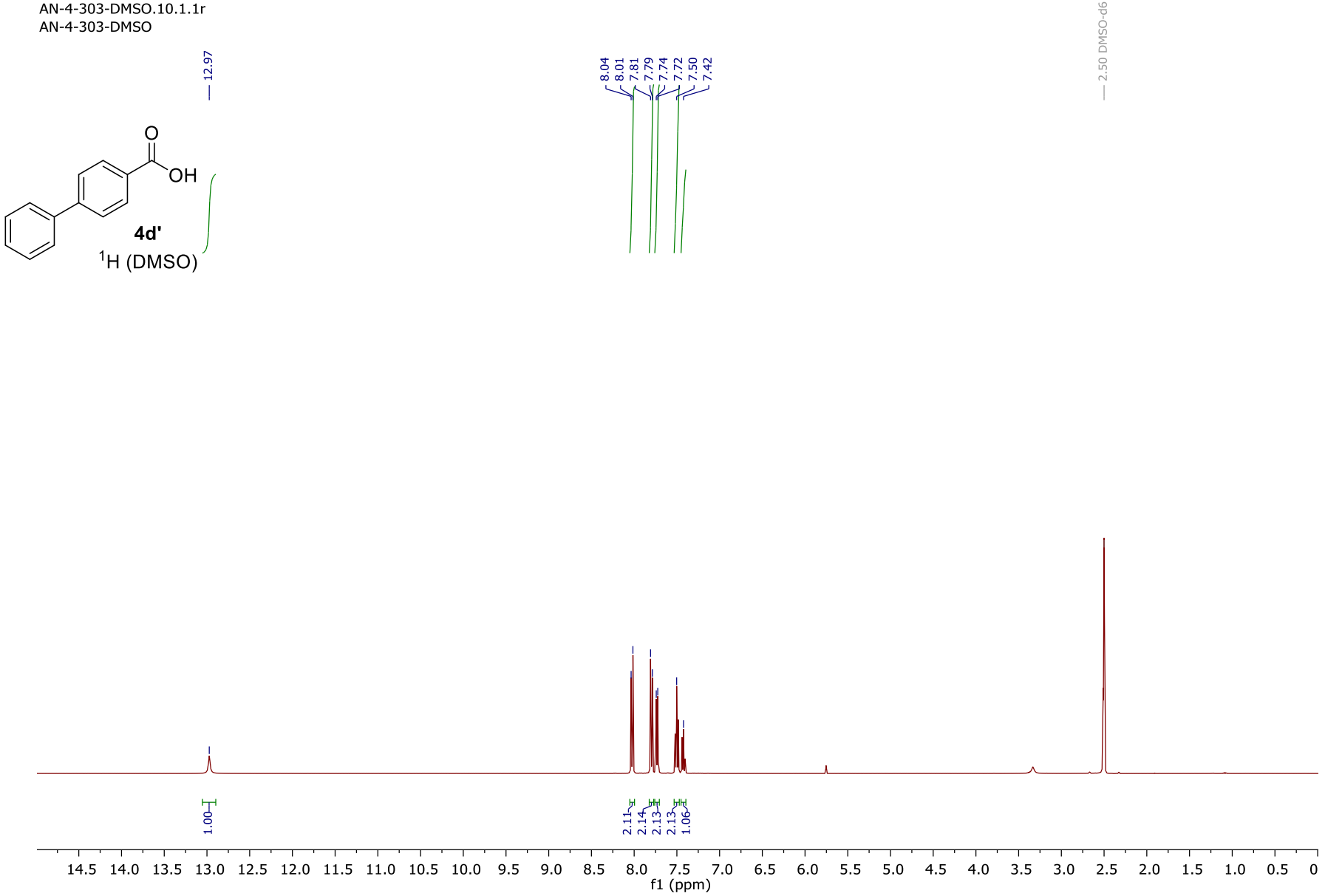
4b'

^{13}C (DMSO_d_6)

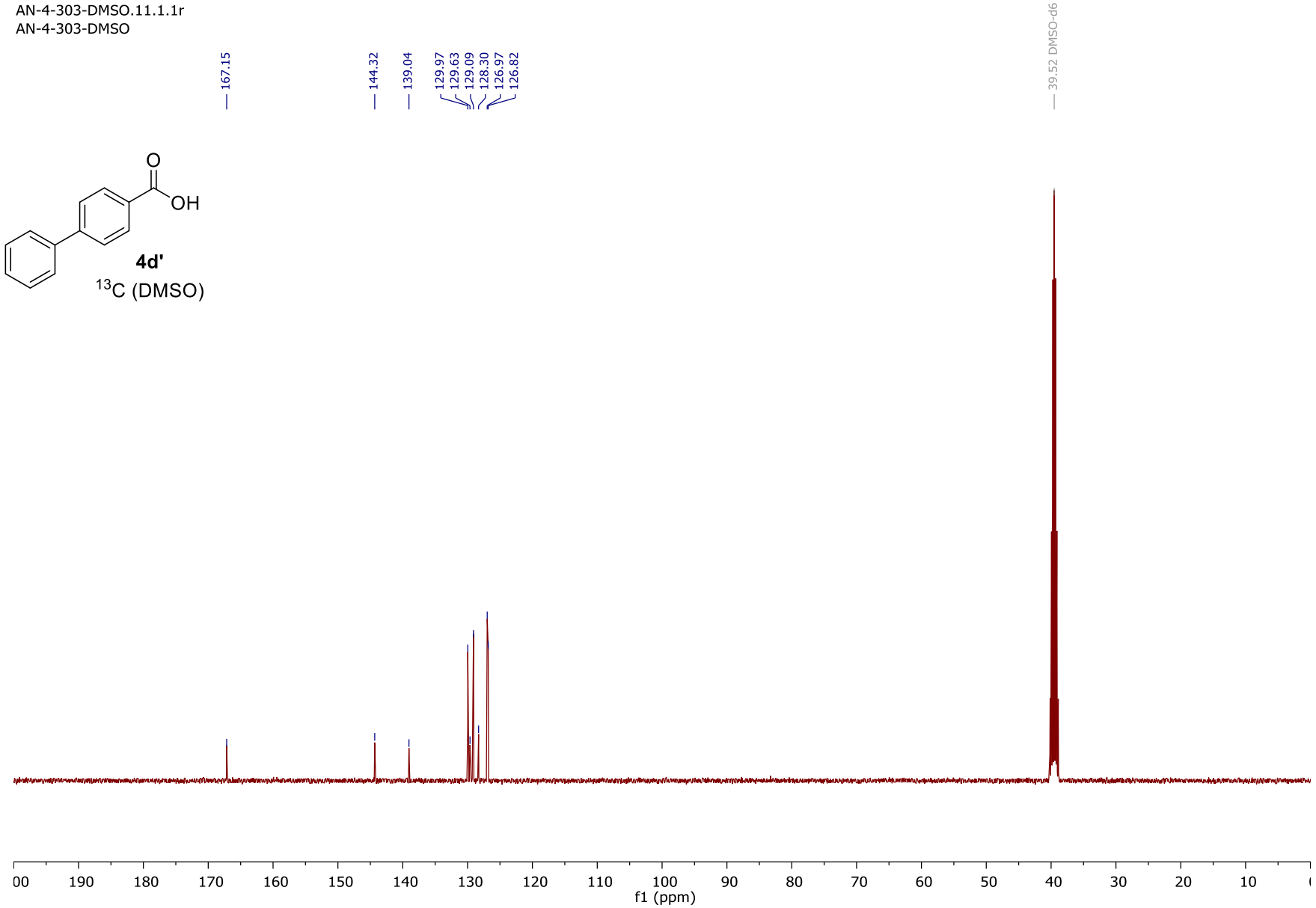

O
OH
NC
4c'
^{1}H (DMSO_d$_6$)
8.09
8.07
7.99
7.97
3.33 H2O
2.50 DMSO
2.00
1.99
f1 (ppm)

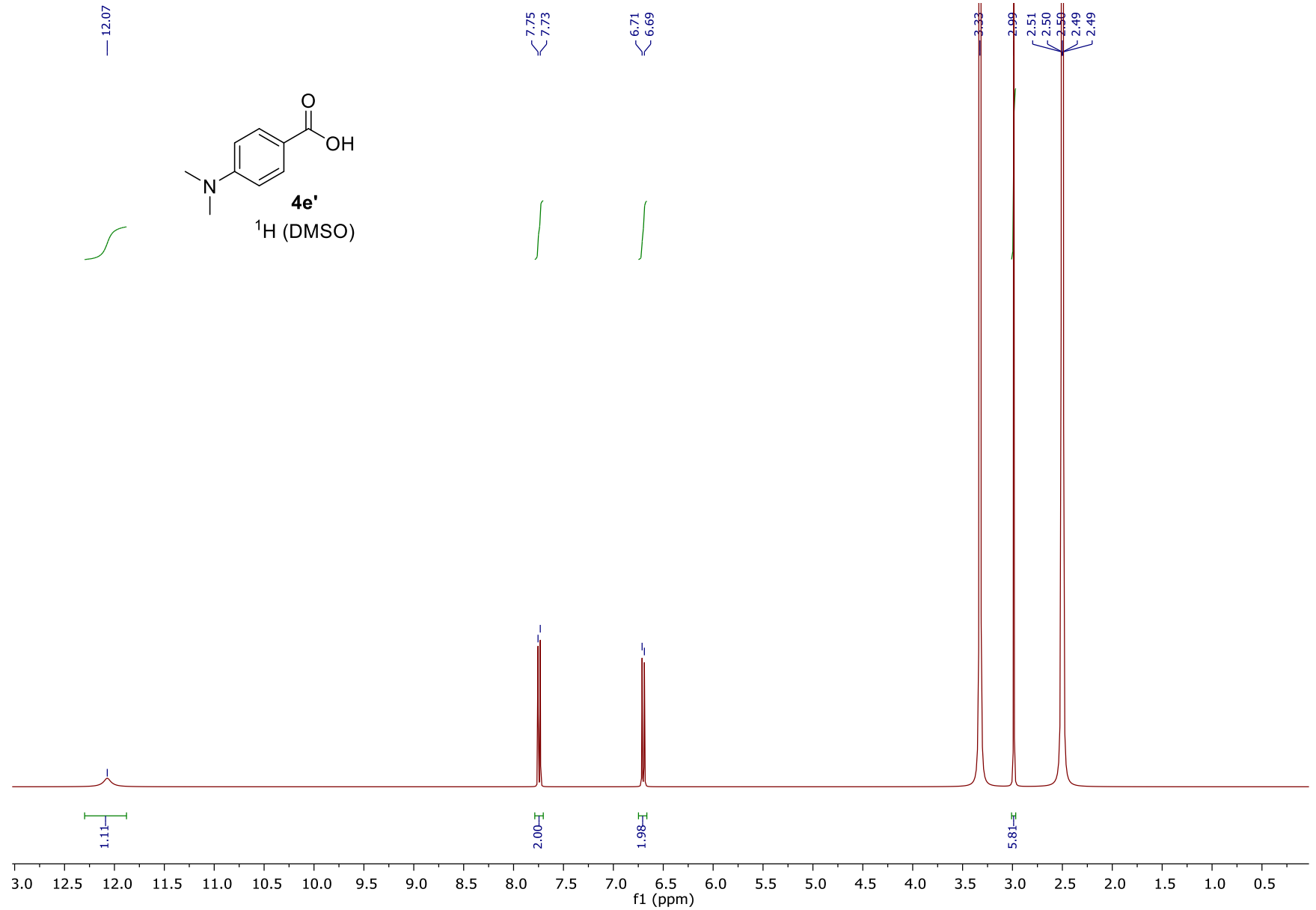

166.09
132.70
129.94
118.21
115.05
39.52 DMSO-d6
O
OH
NC
4c'
13C (DMSO_d6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

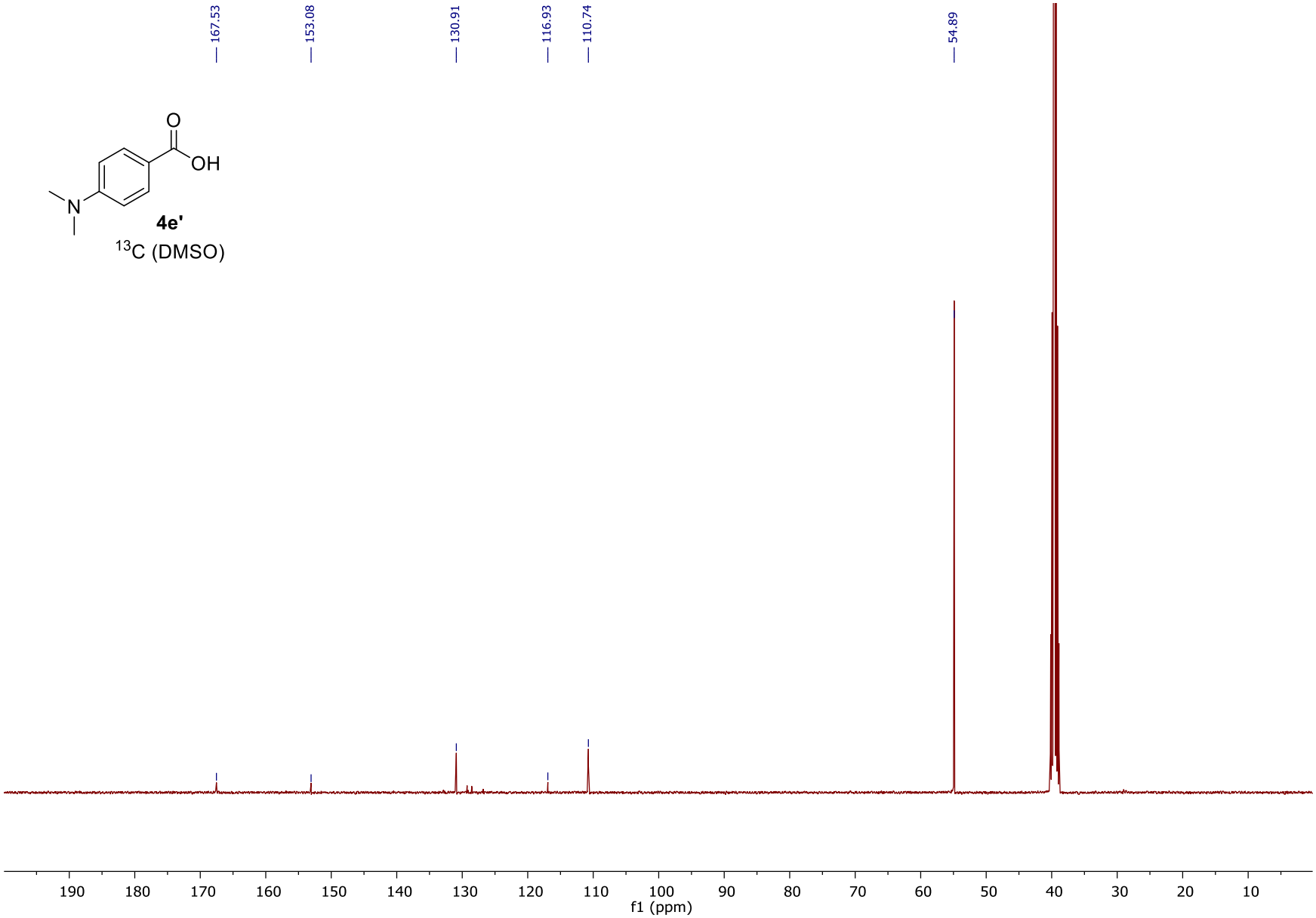
AN-4-303-DMSO.10.1.1r
AN-4-303-DMSO



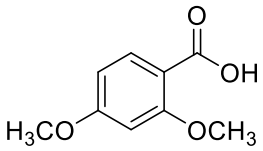
AN-4-303-DMSO.11.1.1r
AN-4-303-DMSO




12.07
7.75
7.73
6.71
6.69
3.33
2.99
2.51
2.50
2.50
2.49
2.49
O
OH
N
4e'
1H (DMSO)
1.11
2.00
1.98
5.81
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


167.53
153.08
130.91
116.93
110.74
54.89
O
OH
N
4e'
13C (DMSO)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

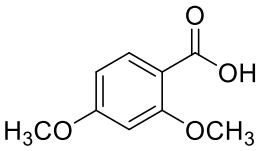
AN-4-295.10.1.1r
AN-4-295



4f'

^1H ($CDCl_3$)

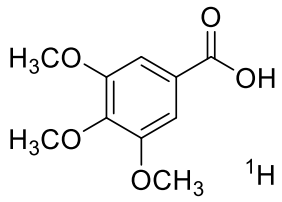
AN-4-295.30.1.1r
AN-4-295



4f'

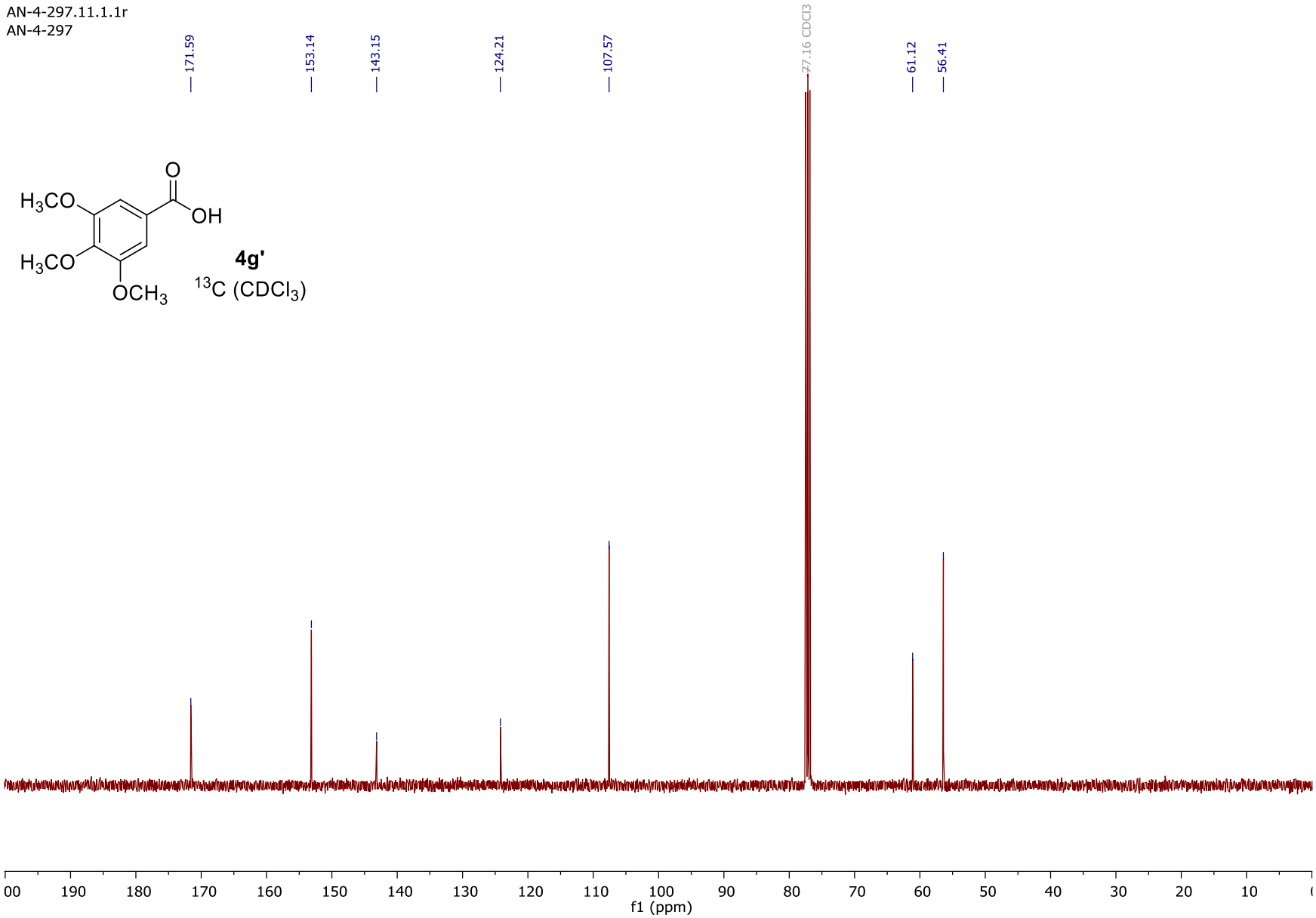
^{13}C ($CDCl_3$)

AN-4-297.10.1.1r
AN-4-297

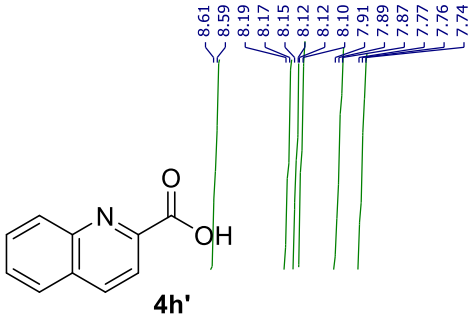


4g'

^1H ($CDCl_3$)


AN-4-297.11.1.1r
AN-4-297
171.59
153.14
143.15
124.21
107.57
77.16 CDCl3
61.12
56.41
H3CO
H3CO
OCH3
O
OH
4g'
13C (CDCl3)
f1 (ppm)

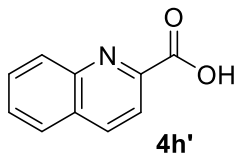
AN-4-299.30.1.1r
AN-4-299



4h'

^{1}H (DMSO)

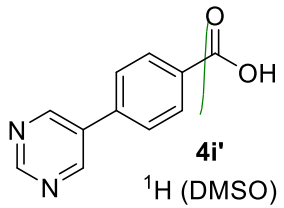
AN-4-299.41.1.1r
AN-4-299



4h'

^{13}C (DMSO)

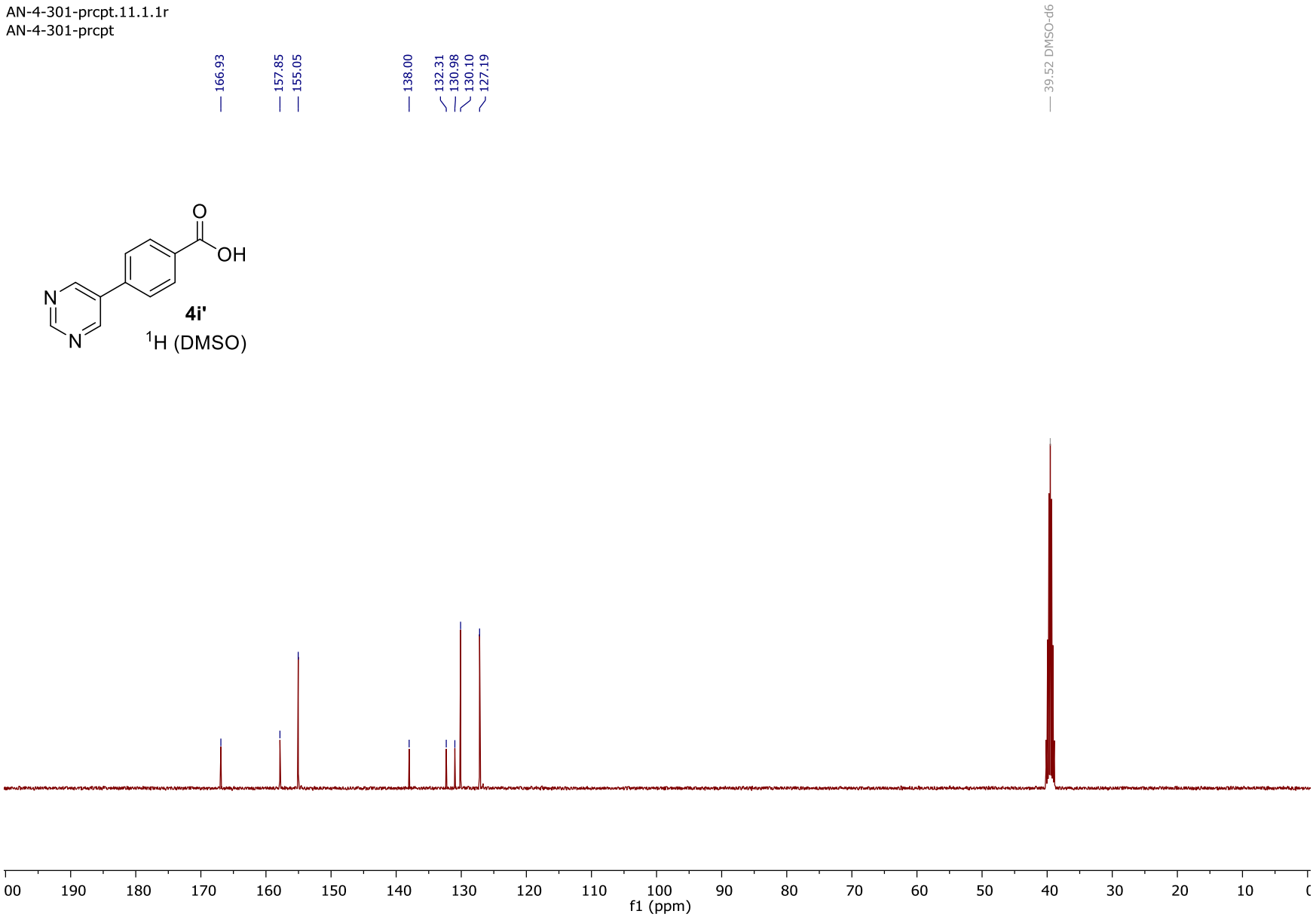
AN-4-301-prcpt.10.1.1r
AN-4-301-prcpt



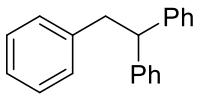
4i'

^{1}H (DMSO)

AN-4-301-prcpt.11.1.1r
AN-4-301-prcpt



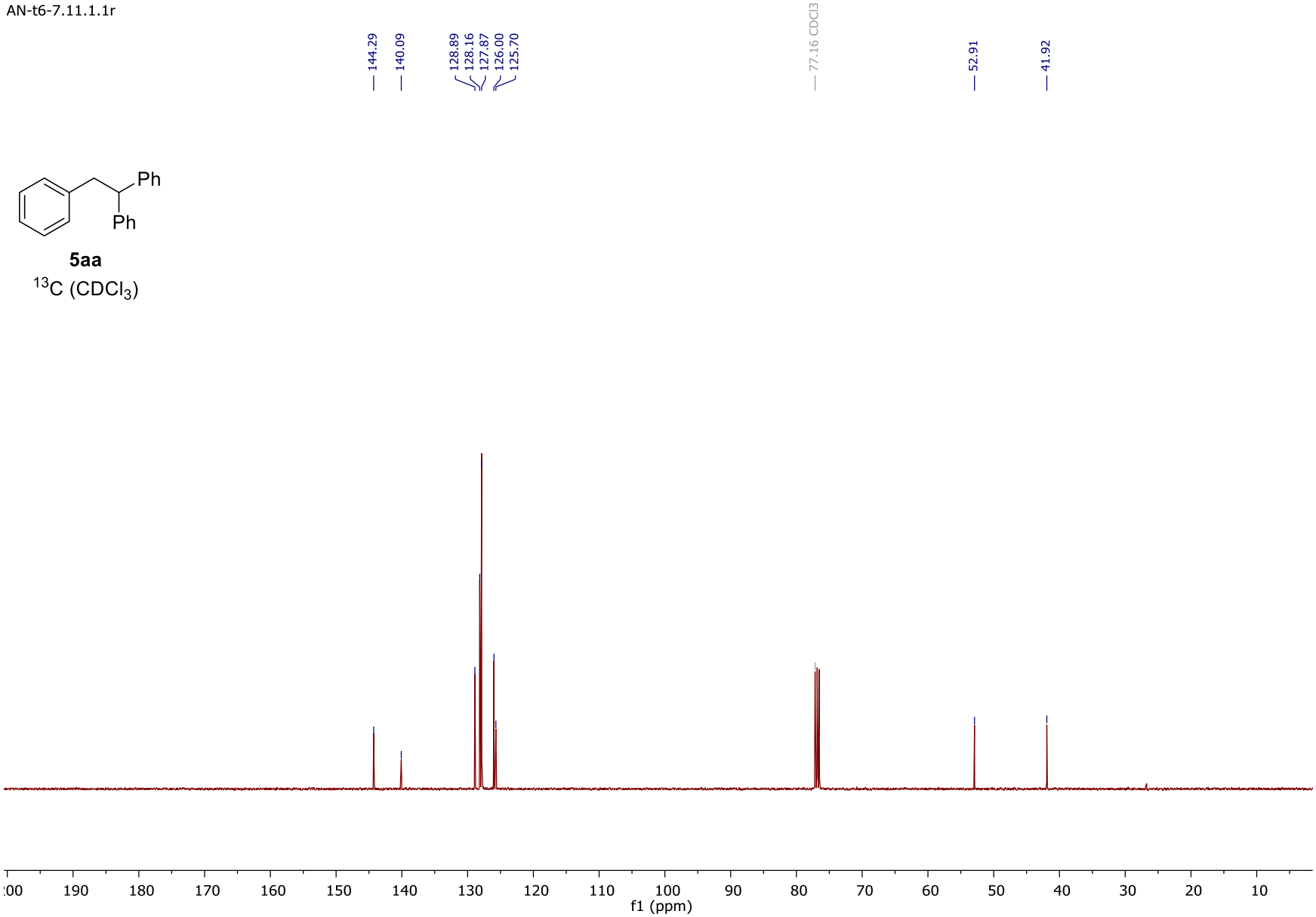
AN-t6-7.10.1.1r



5aa

^1H ($CDCl_3$)

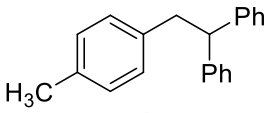
AN-t6-7.11.1.1r



5aa

^{13}C ($CDCl_3$)

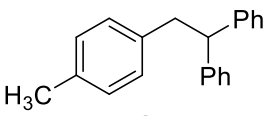
AN-3-252.20.1.1r



5ba

^1H ($CDCl_3$)

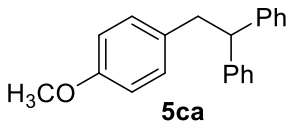
AN-3-252.21.1.1r



5ba

^{13}C ($CDCl_3$)

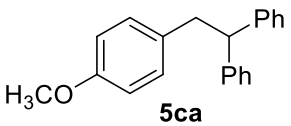
AN-3-260.10.1.1r



5ca

^1H ($CDCl_3$)

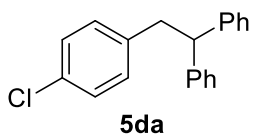
AN-3-260.11.1.1r



5ca

^{13}C ($CDCl_3$)

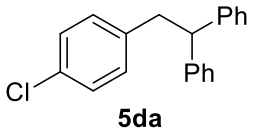
AN-3-243-SI.20.1.1r
AN-3-243-SI



5da

^1H ($CDCl_3$)

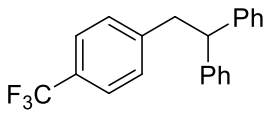
AN-3-243.41.1.1r



5da

^{13}C ($CDCl_3$)

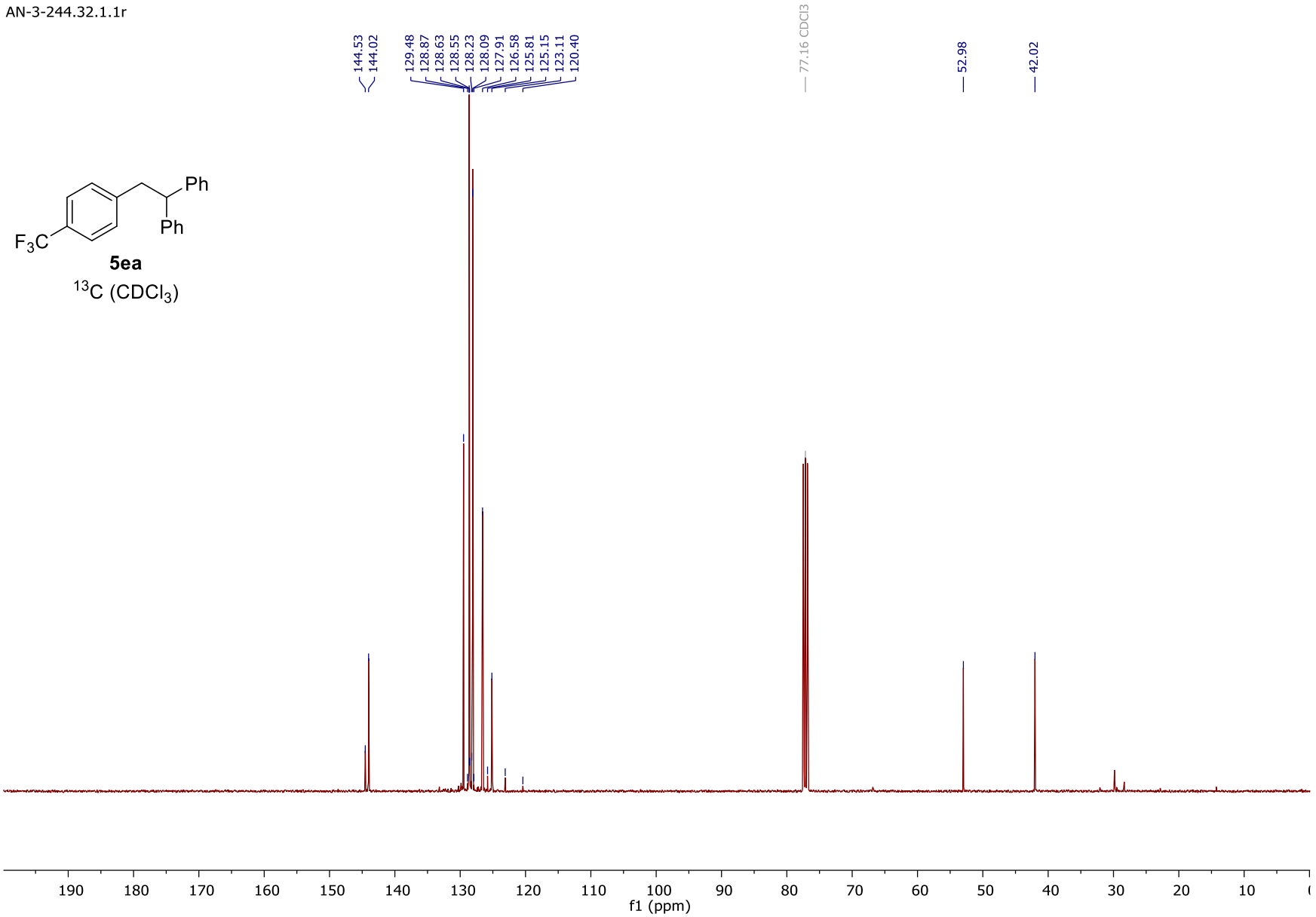
AN-3-244.40.1.1r



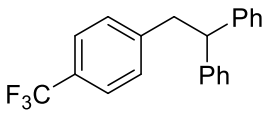
5ea

^{1}H ($CDCl_3$)

AN-3-244.32.1.1r



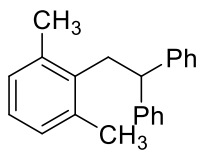
AN-3-244.31.1.1r



5ea

^{19}F ($CDCl_3$)

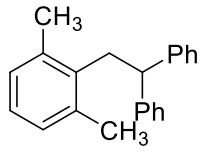
AN-4-294.10.1.1r



5fa

^1H ($CDCl_3$)

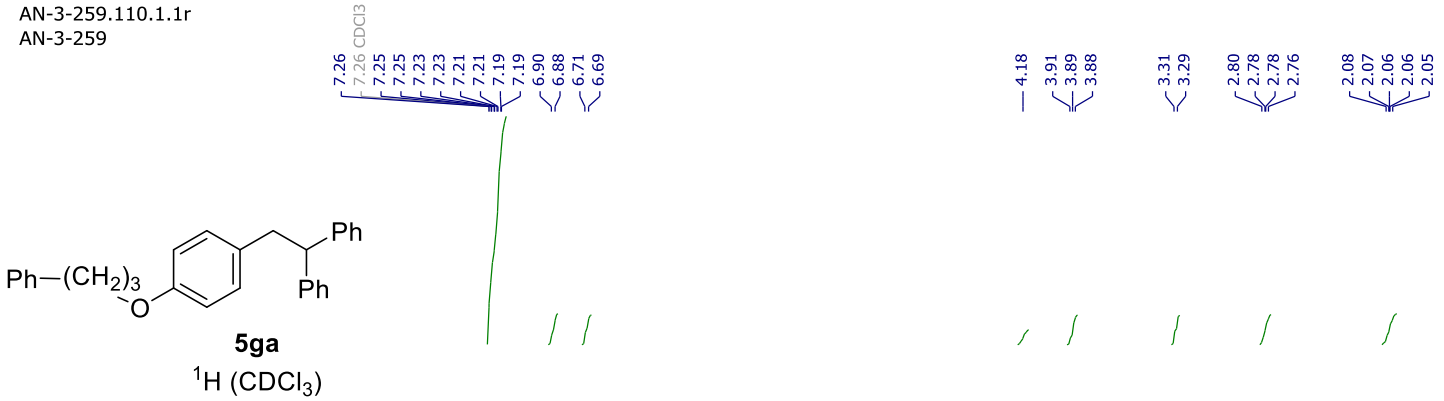
AN-4-294.11.1.1r



5fa

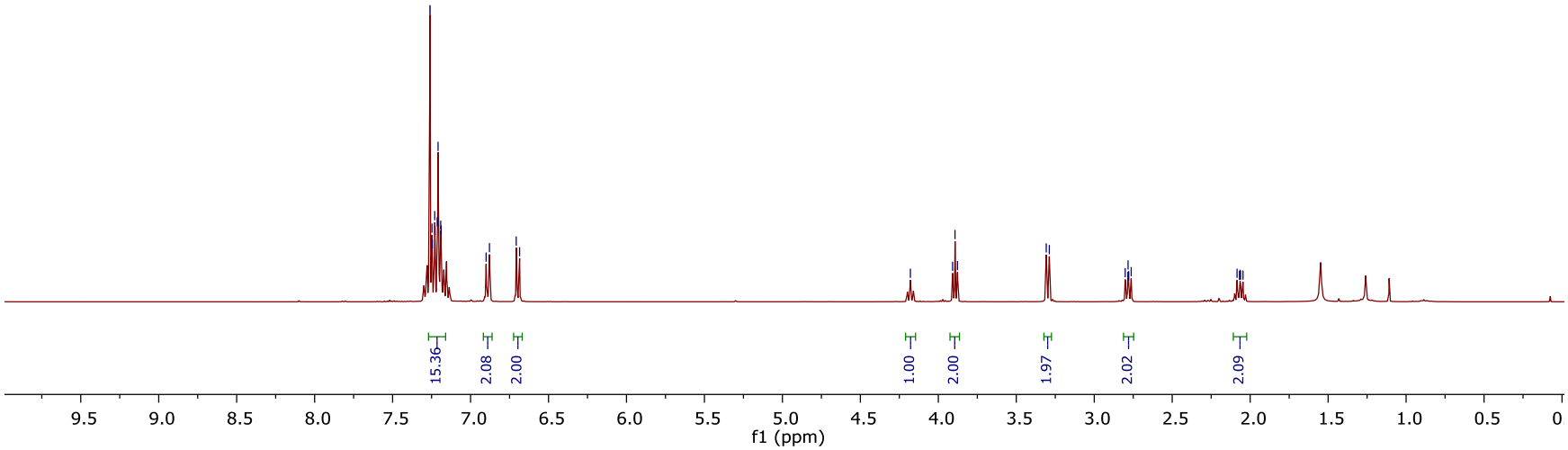
^{13}C ($CDCl_3$)

AN-3-259.110.1.1r
AN-3-259

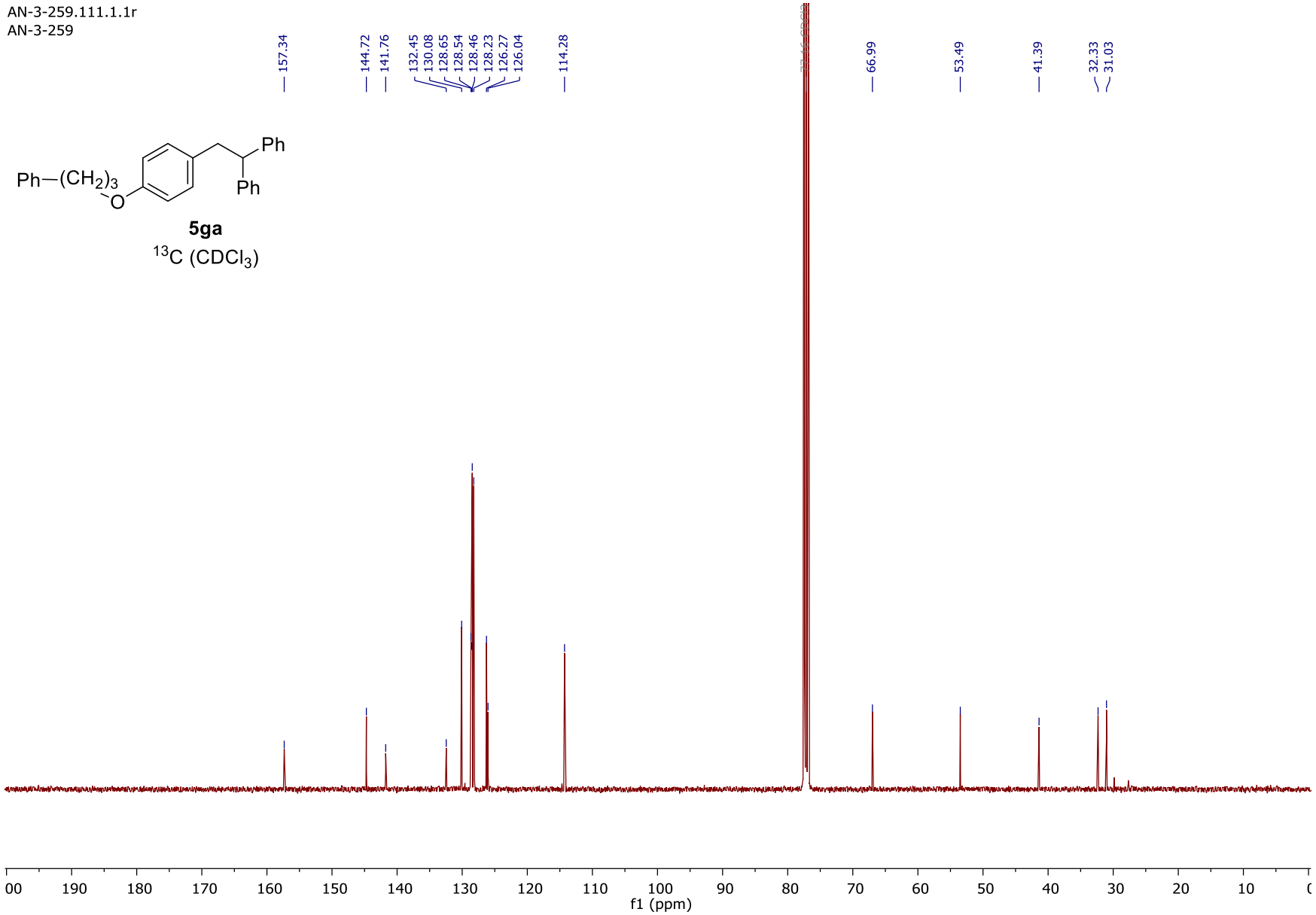


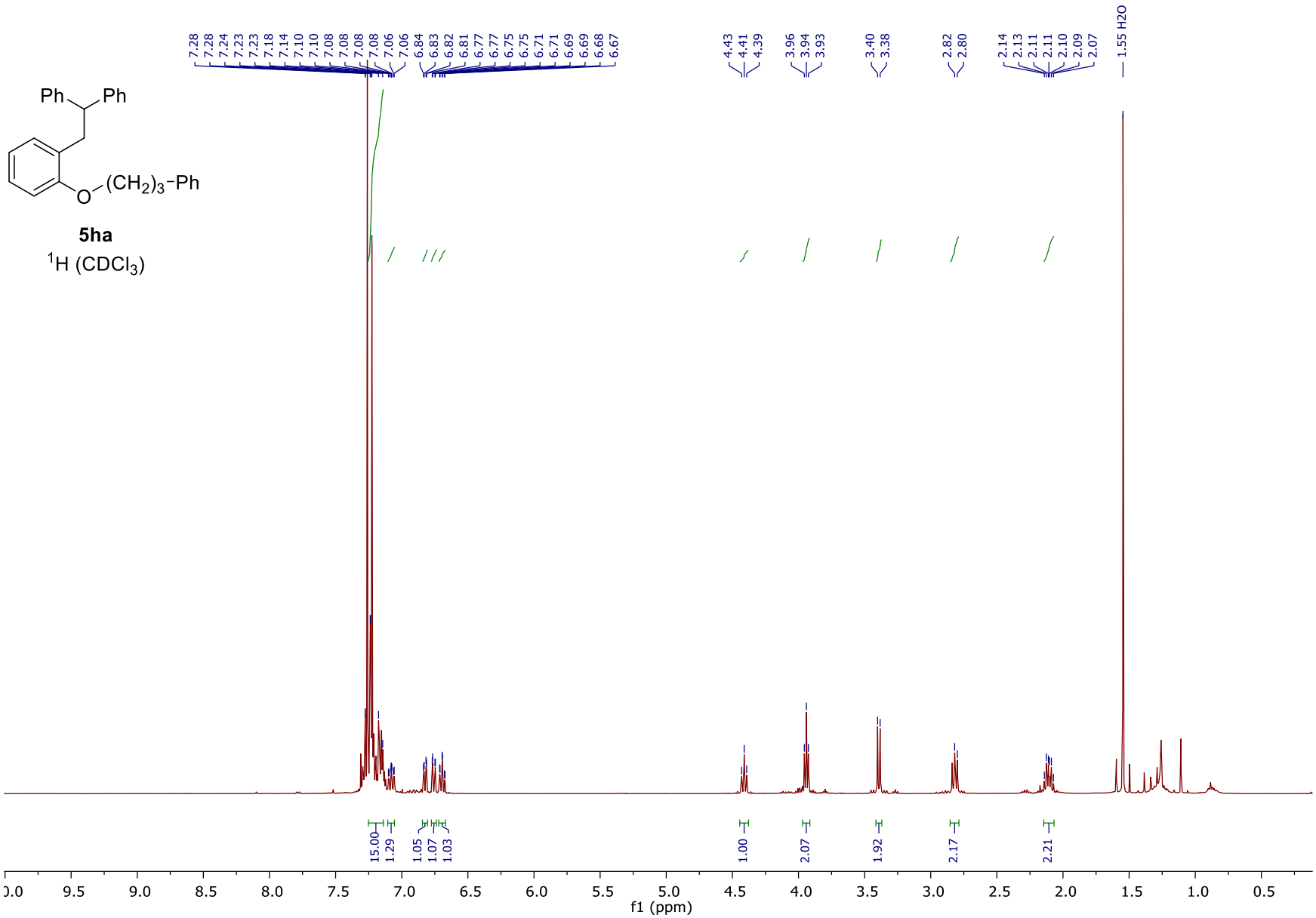
5ga

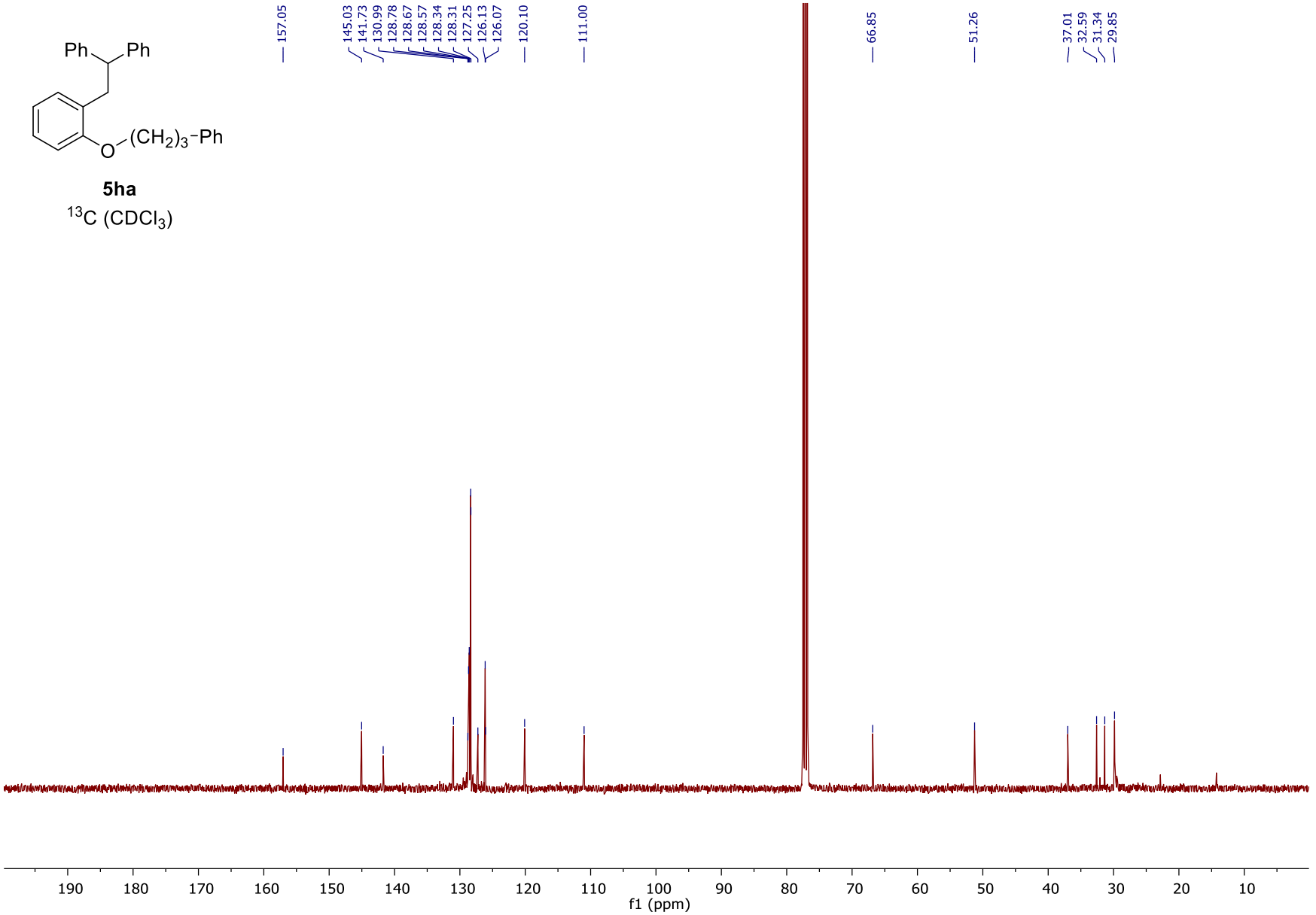
^{1}H ($CDCl_3$)



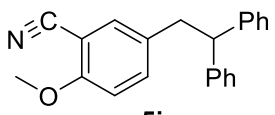
AN-3-259.111.1.1r
AN-3-259




Ph
Ph
O
(CH2)3-Ph
5ha
1H (CDCl3)
7.28
7.28
7.24
7.23
7.23
7.18
7.14
7.10
7.10
7.08
7.08
7.08
7.08
7.06
7.06
6.84
6.83
6.82
6.81
6.77
6.77
6.75
6.75
6.71
6.71
6.69
6.69
6.68
6.67
4.43
4.41
4.39
3.96
3.94
3.93
3.40
3.38
2.82
2.80
2.14
2.13
2.11
2.11
2.10
2.09
2.07
1.55 H2O
15.00
1.29
1.05
1.07
1.03
1.00
2.07
1.92
2.17
2.21
f1 (ppm)

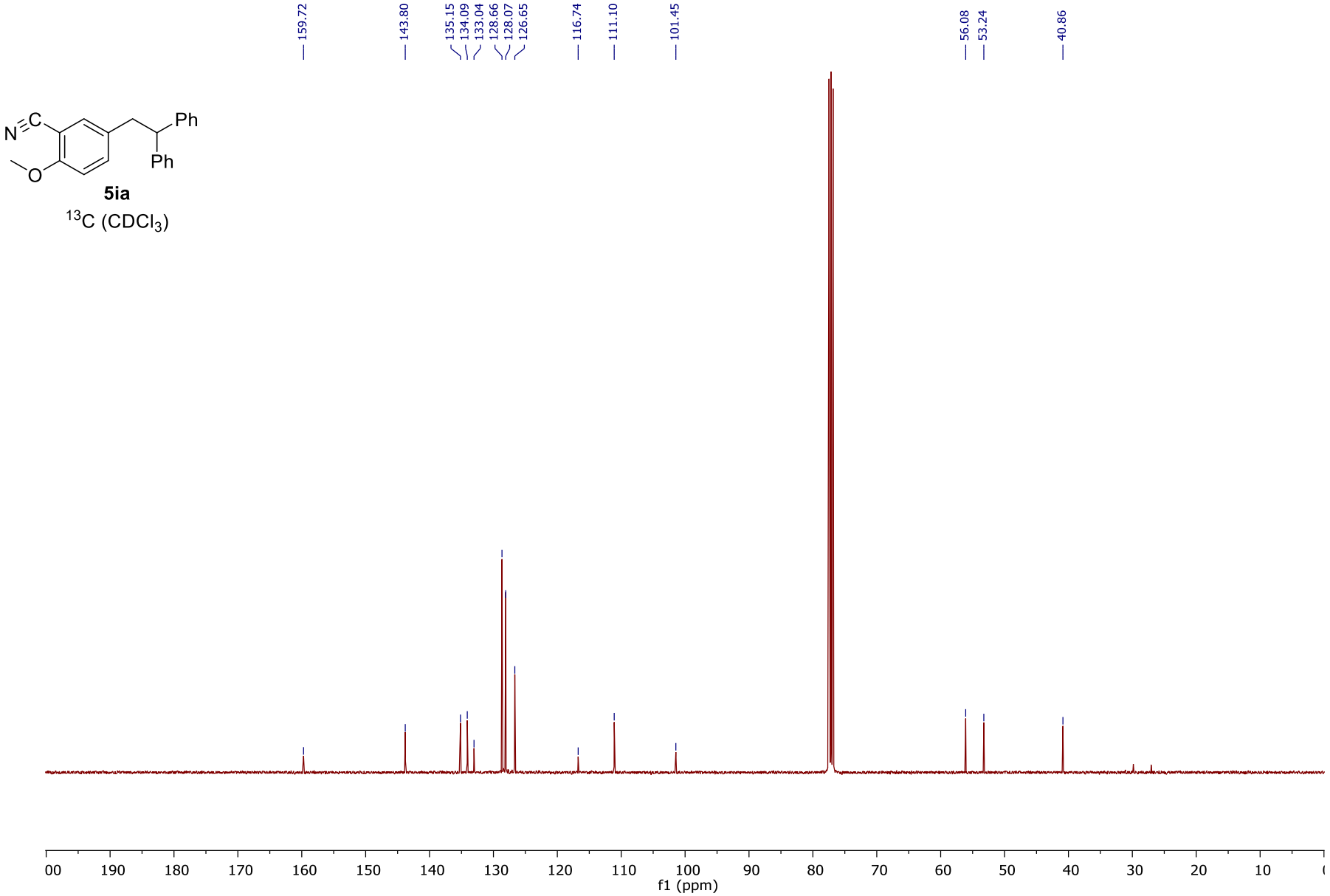

Ph
Ph
O
(CH2)3-Ph
5ha
13C (CDCl3)
157.05
145.03
141.73
130.99
128.78
128.67
128.57
128.34
128.31
127.25
126.13
126.07
120.10
111.00
66.85
51.26
37.01
32.59
31.34
29.85
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

AN-3-250-2-F2.20.1.1r

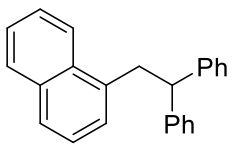


5ia

^1H ($CDCl_3$)


159.72
143.80
135.15
134.09
133.04
128.66
128.07
126.65
116.74
111.10
101.45
56.08
53.24
40.86
N
C
O
Ph
Ph
5ia
13C (CDCl3)
f1 (ppm)

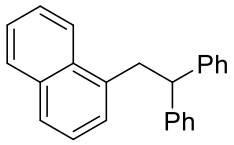
AN-4-293.10.1.1r



5ja

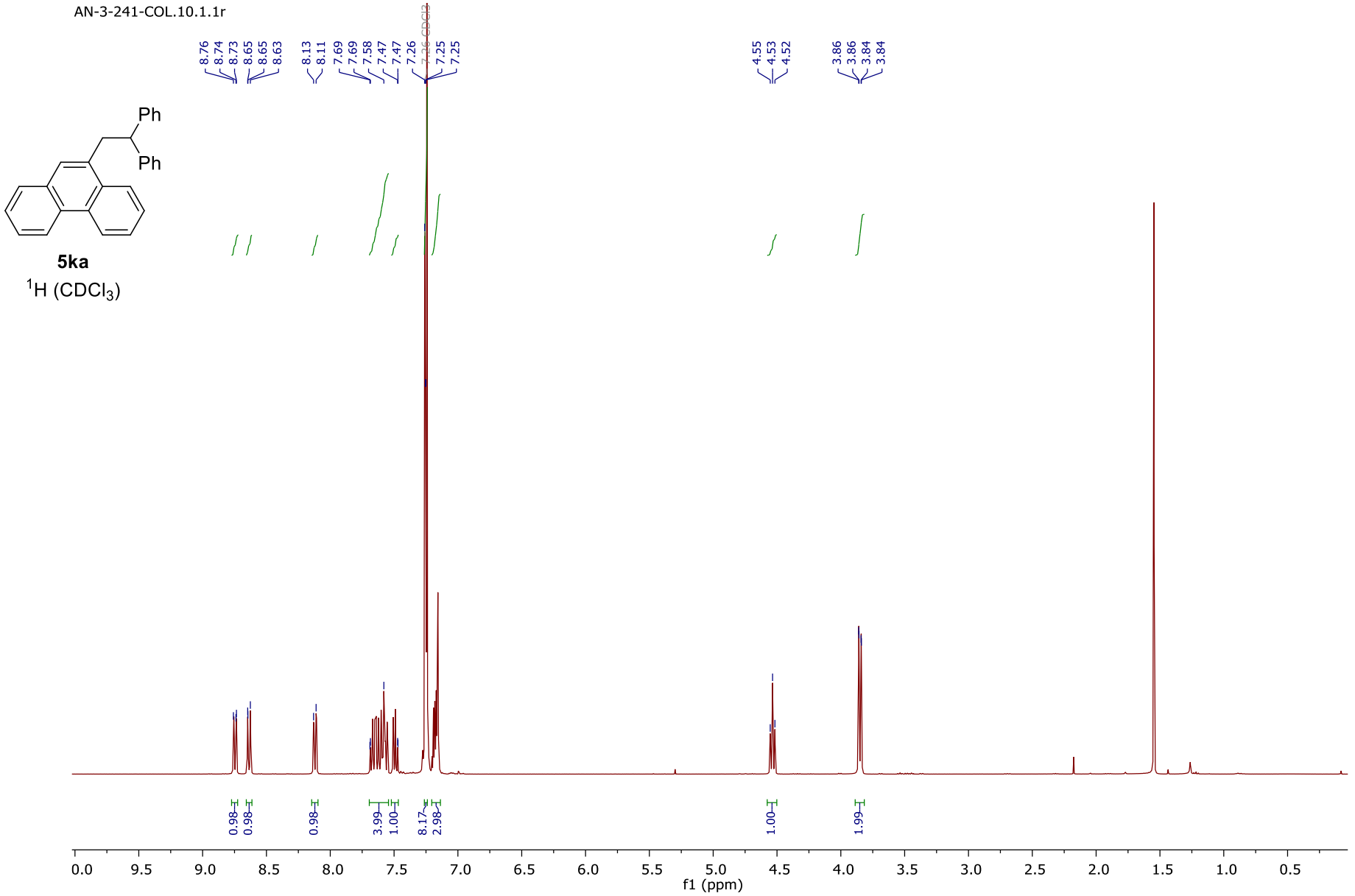
^1H ($CDCl_3$)

AN-4-293.11.1.1r

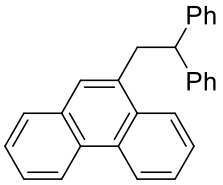


5ja

^{13}C ($CDCl_3$)


AN-3-241-COL.10.1.1r
8.76
8.74
8.73
8.65
8.65
8.63
8.13
8.11
7.69
7.69
7.58
7.47
7.47
7.26
7.25
7.25
4.55
4.53
4.52
3.86
3.86
3.84
3.84
Ph
Ph
5ka
1H (CDCl3)
0.98
0.98
0.98
3.99
1.00
8.17
2.98
1.00
1.99
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

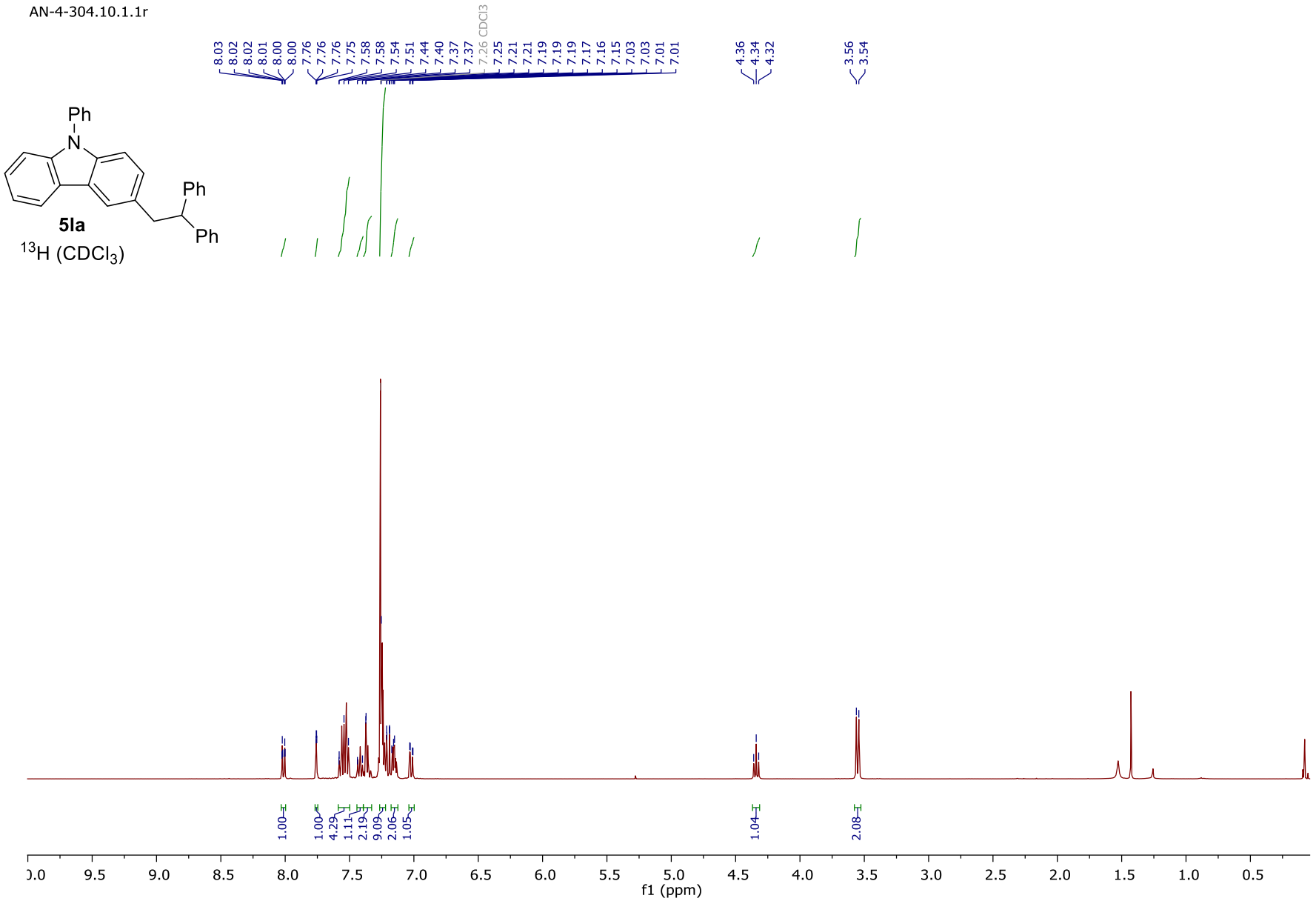
AN-3-241-COL.11.1.1r



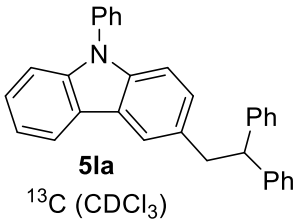
5ka

^{13}C ($CDCl_3$)

AN-4-304.10.1.1r



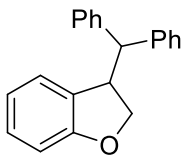
AN-4-304.11.1.1r



5la

^{13}C ($CDCl_3$)

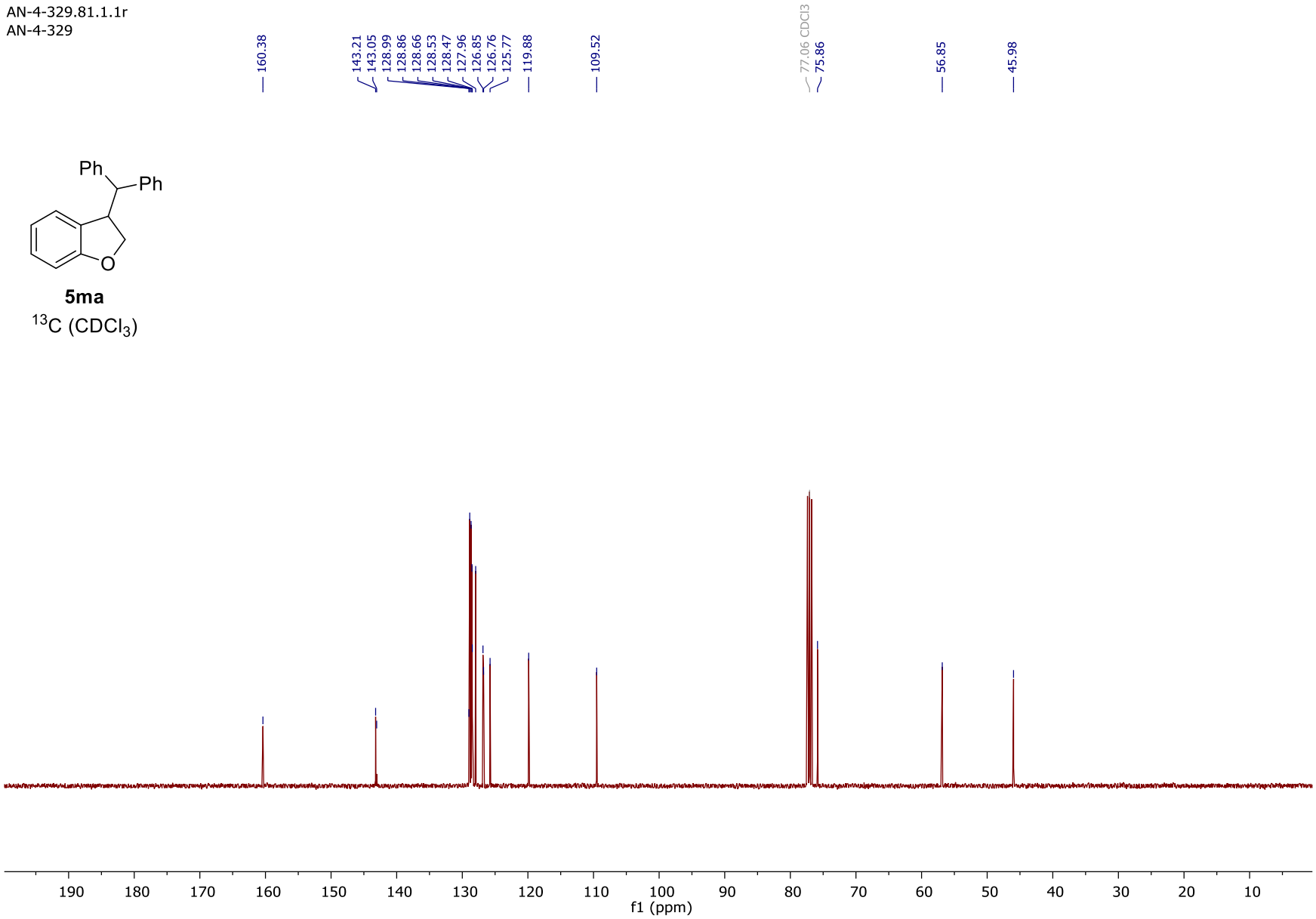
AN-4-329.80.1.1r
AN-4-329



5ma

^1H ($CDCl_3$)

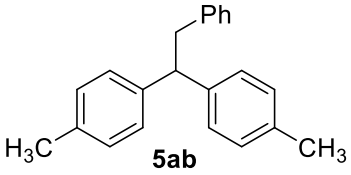
AN-4-329.81.1.1r
AN-4-329



5ma

^{13}C ($CDCl_3$)

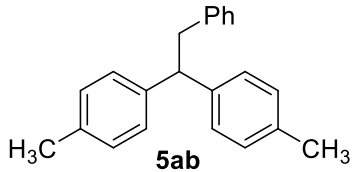
AN-DL7015C.10.1.1r
AN-DL7015C



5ab

^1H ($CDCl_3$)

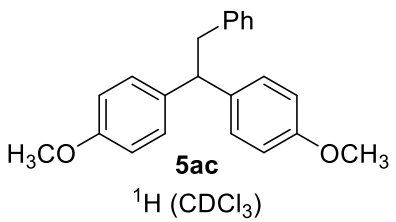
AN-DL7015C.11.1.1r
AN-DL7015C



5ab

^{13}C ($CDCl_3$)

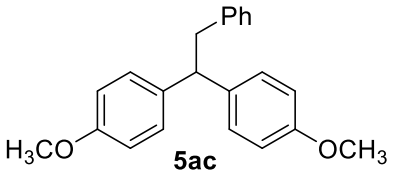
AN-DL030-3.90.1.1r
AN-DL030-3



5ac

^{1}H ($CDCl_3$)

AN-DL030-3.91.1.1r
AN-DL030-3



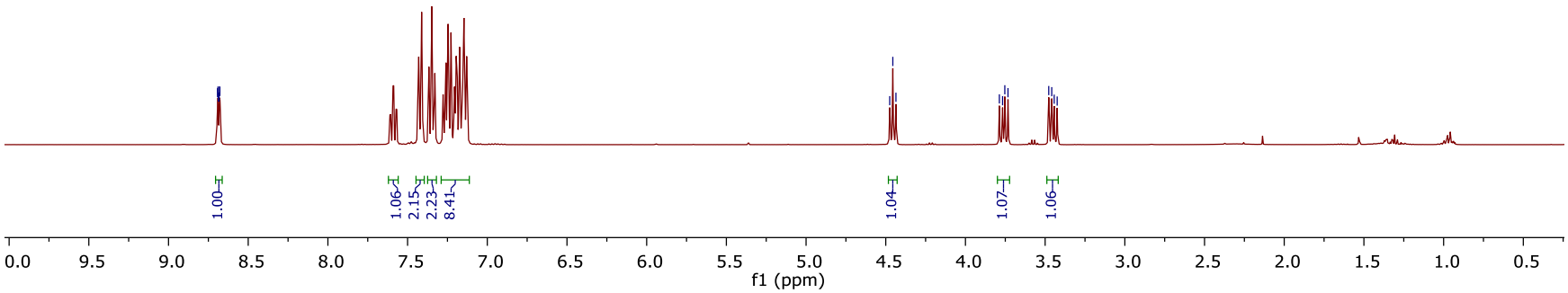
5ac

^{13}C ($CDCl_3$)

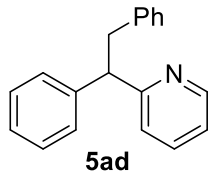
DL7_010C.42.fid
DL7_010C
final
3-4

5ad

^1H ($CDCl_3$)



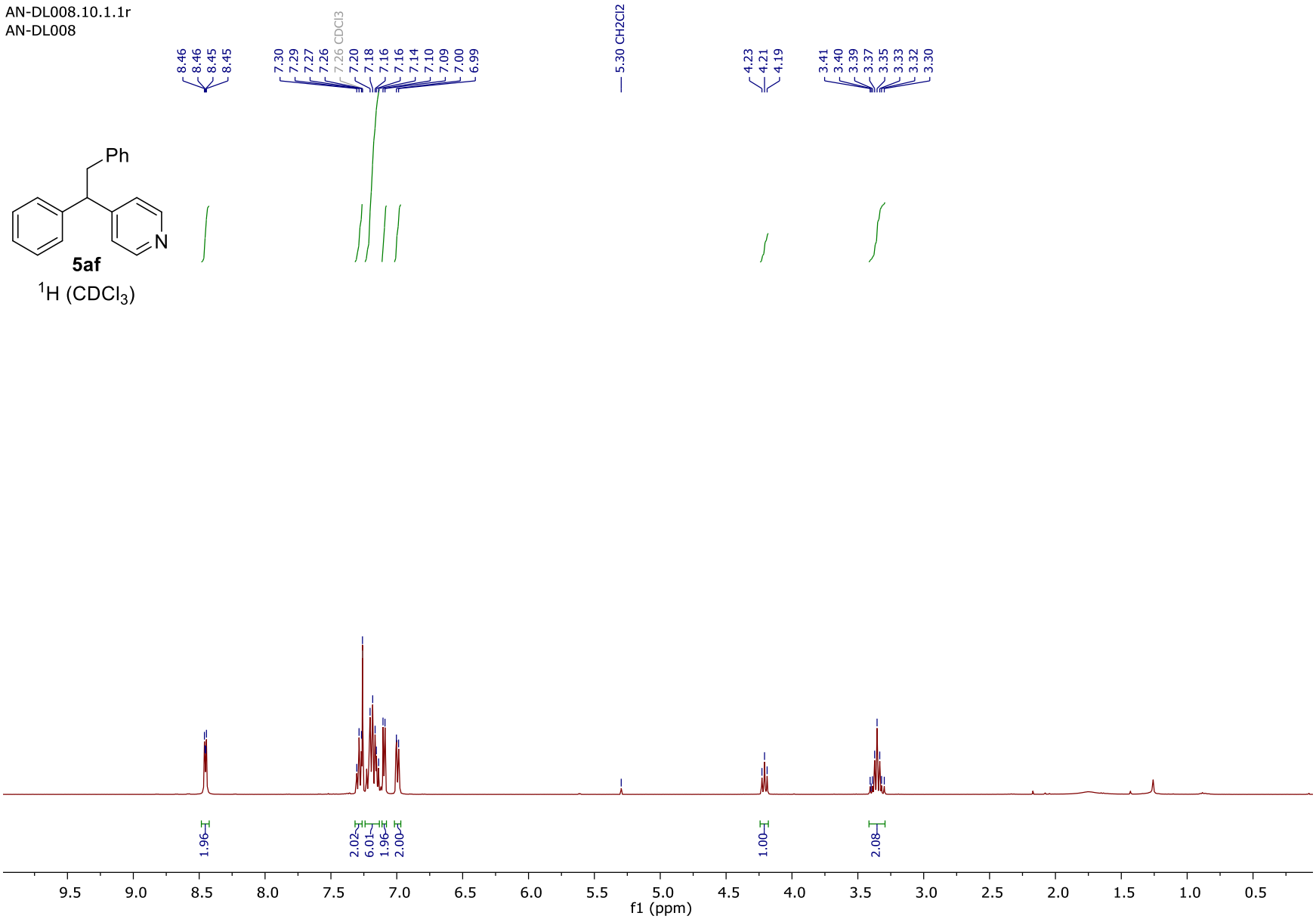
DL7_010C.41.fid
DL7_010C
final
3-4



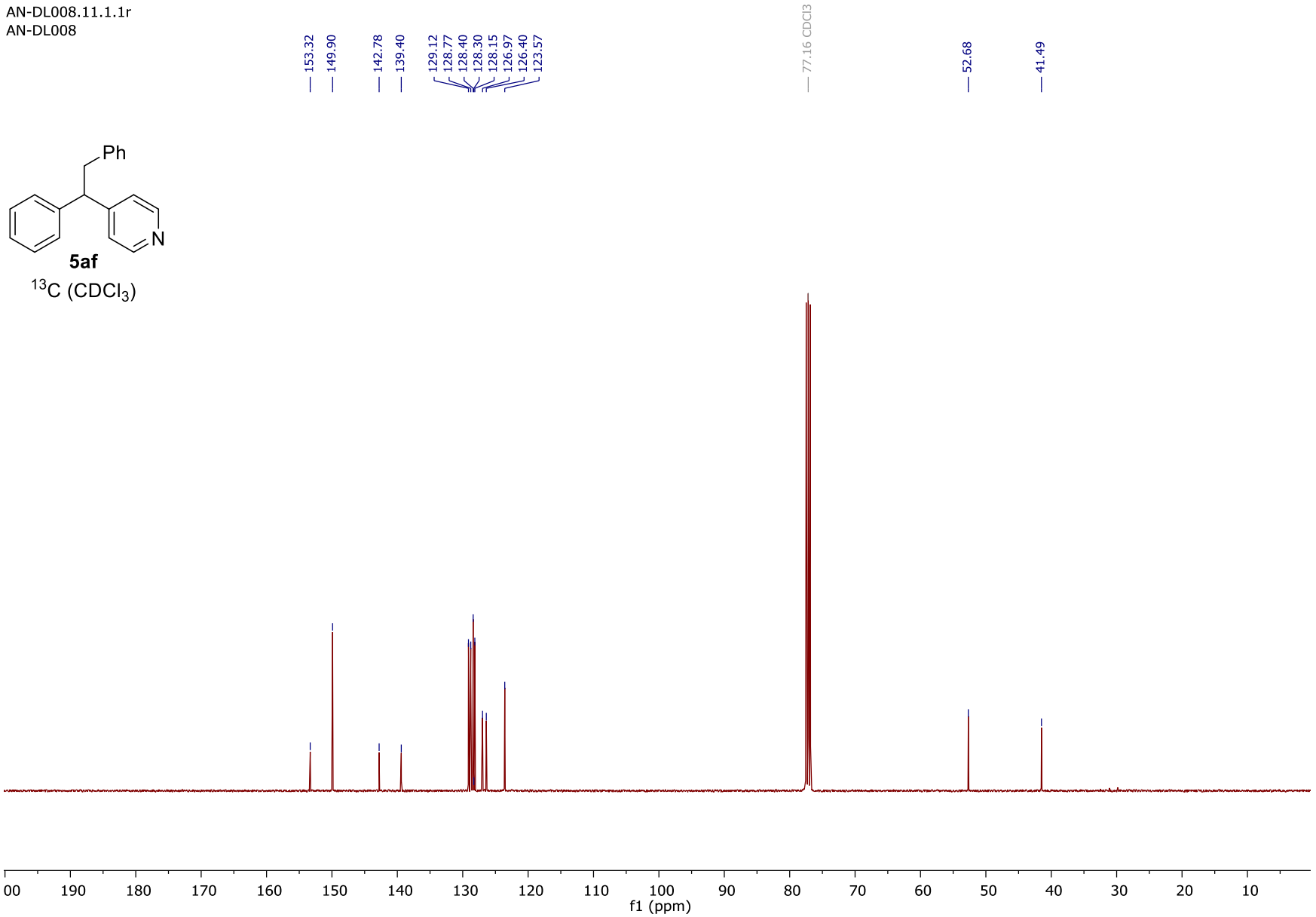
5ad

^1H ($CDCl_3$)

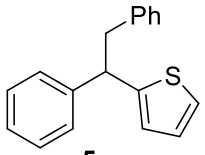
AN-DL008.10.1.1r
AN-DL008



AN-DL008.11.1.1r
AN-DL008



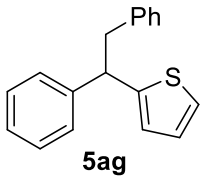
DL7_013C.40.1.1r
DL7_013C
final + etuve all night



5ag

^1H ($CDCl_3$)

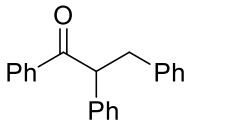
DL7_013C.41.1.1r
DL7_013C
final + etuve all night



5ag

^{13}C ($CDCl_3$)

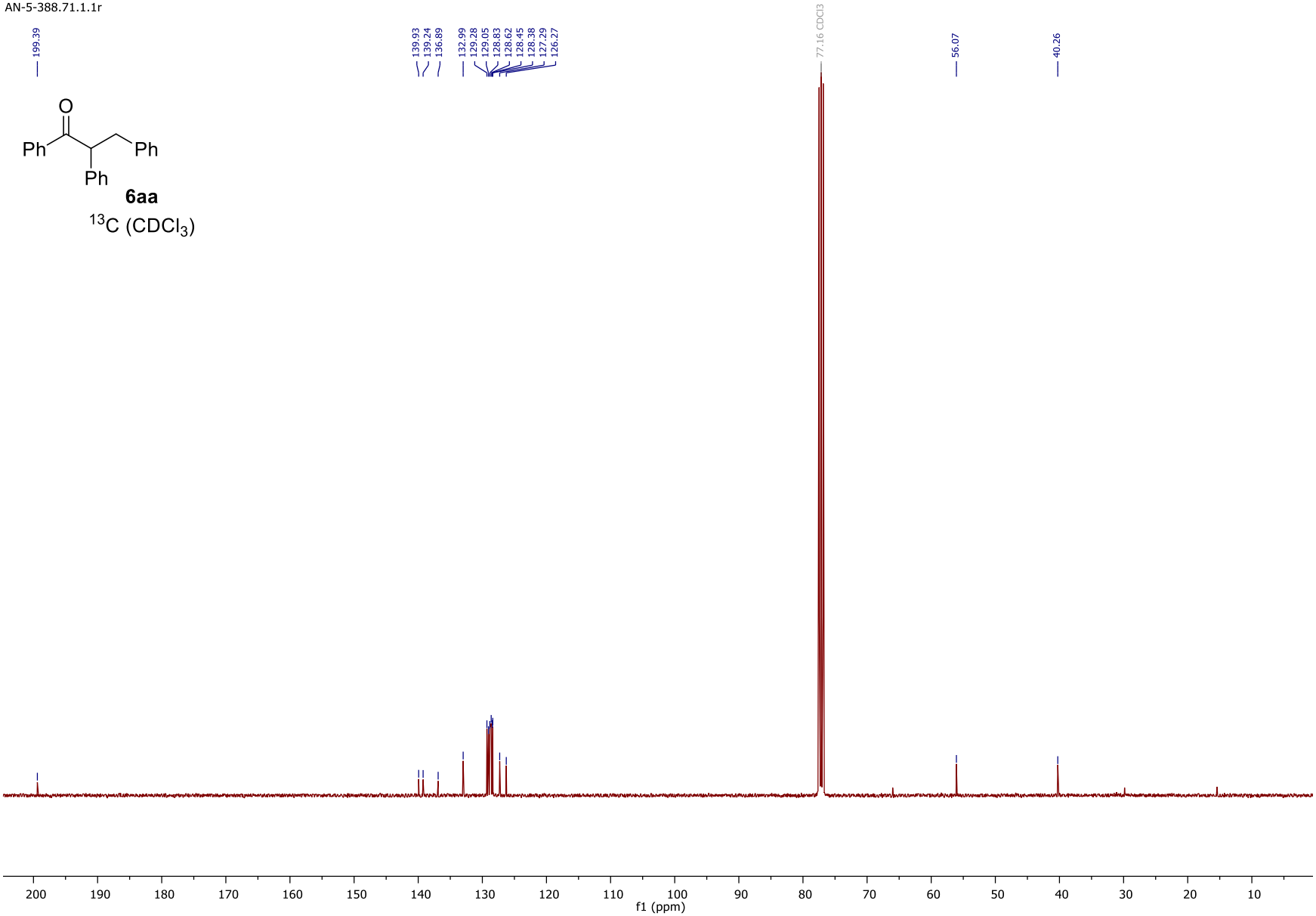
AN-5-388.60.1.1r
AN-5-388-B2-T4-6



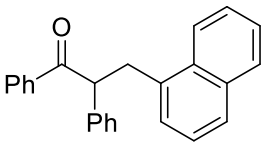
6aa

^1H ($CDCl_3$)

AN-5-388.71.1.1r



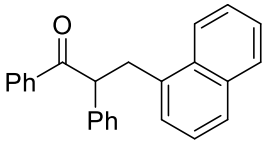
AN-5-389.80.1.1r
AN-5-389B2-T9-13



6ja

^1H ($CDCl_3$)

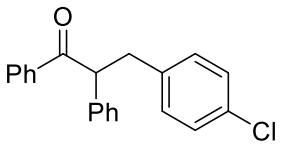
AN-5-389.100.1.1r



6ja

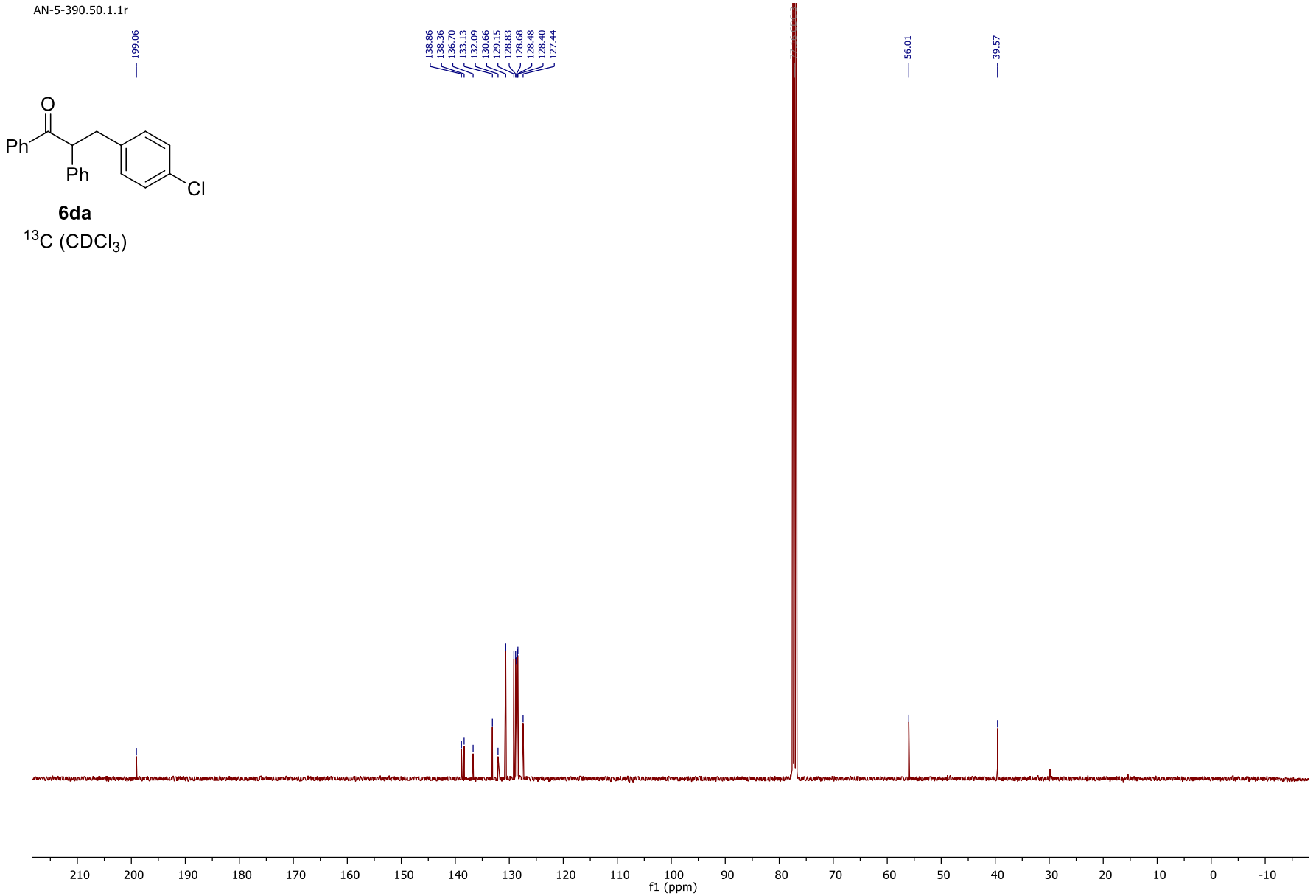
^{1}H ($CDCl_3$)

AN-5-390.40.1.1r
AN-5-390-B2-T7-13

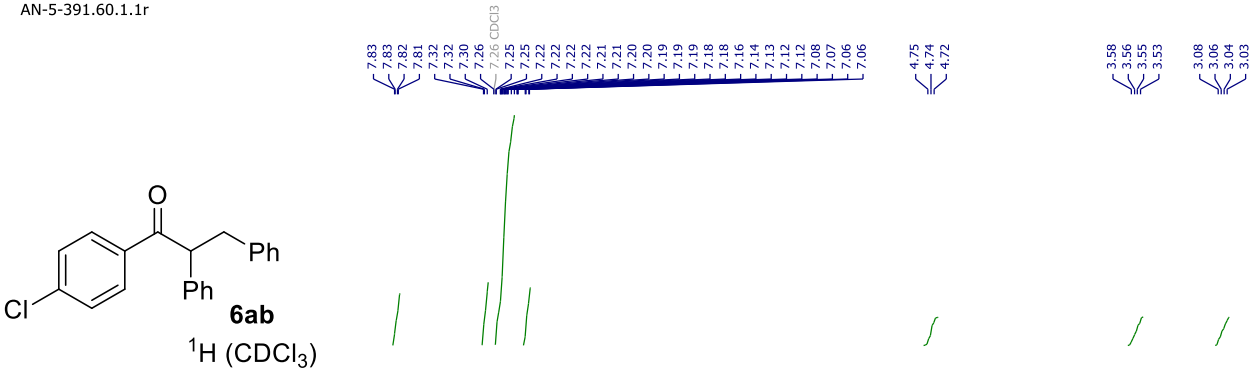


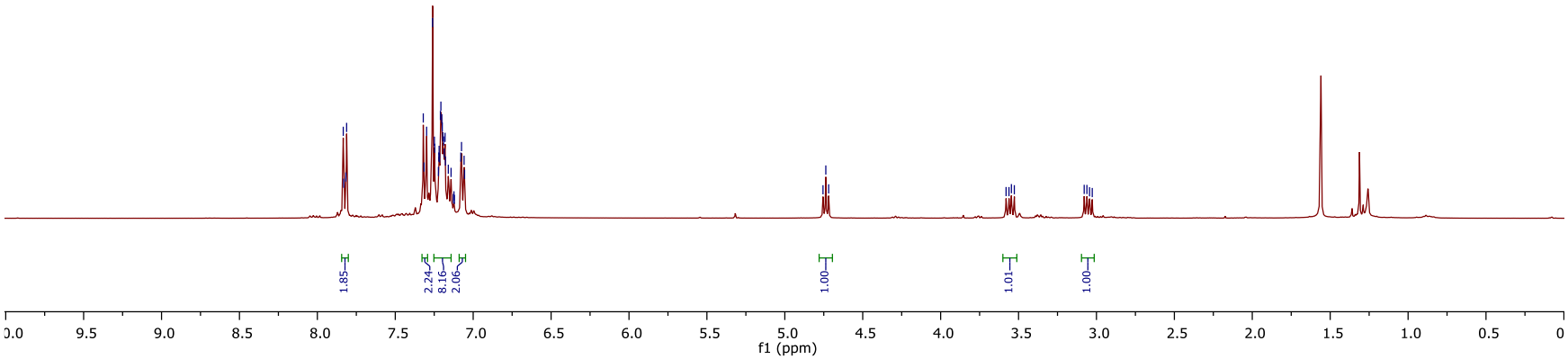
6da

^1H ($CDCl_3$)

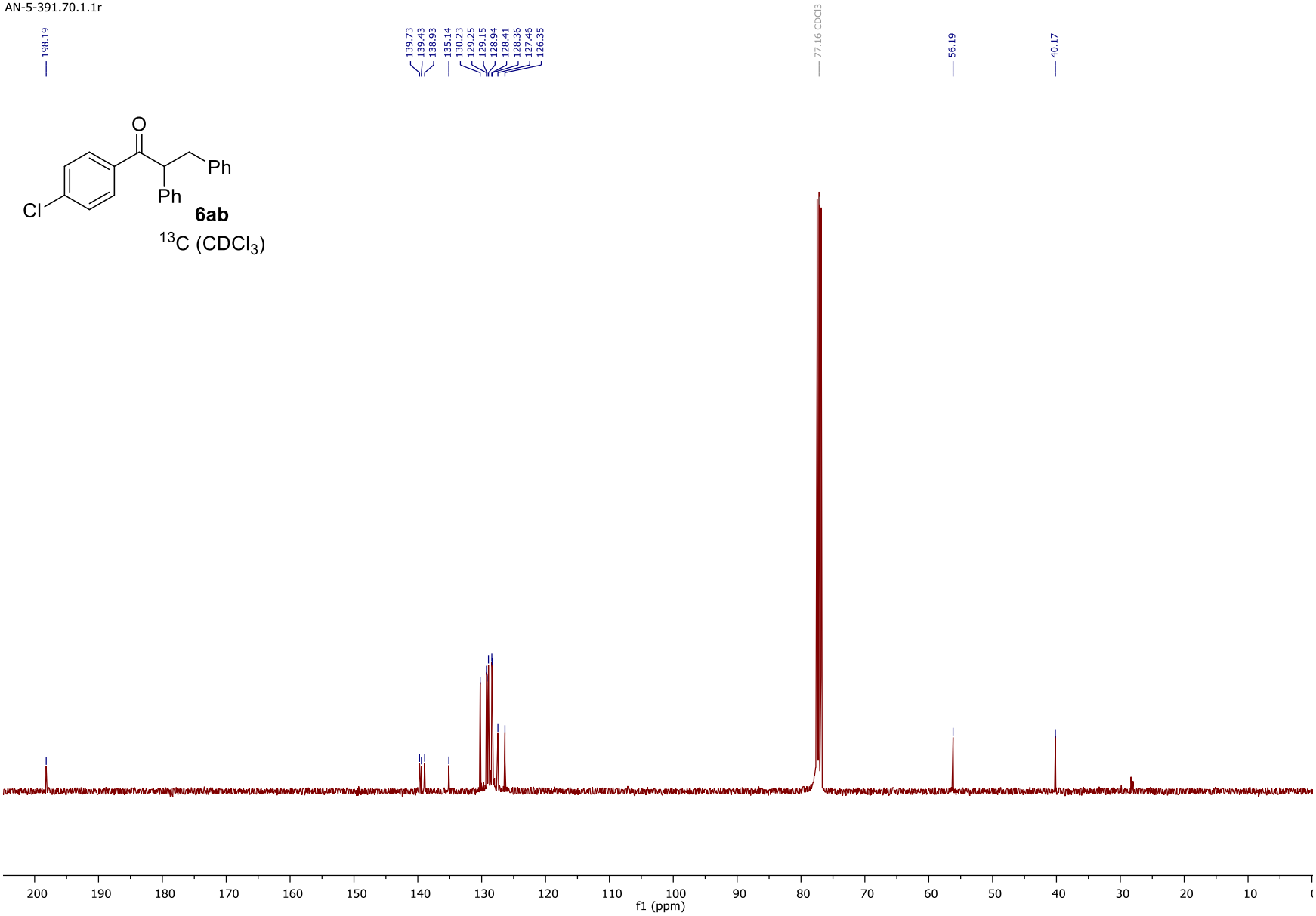

AN-5-390.50.1.1r
199.06
138.86
138.36
136.70
133.13
132.09
130.66
129.15
128.83
128.68
128.48
128.40
127.44
56.01
39.57
O
Ph
Ph
Cl
6da
^{13}C ($CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

AN-5-391.60.1.1r

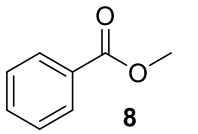




AN-5-391.70.1.1r

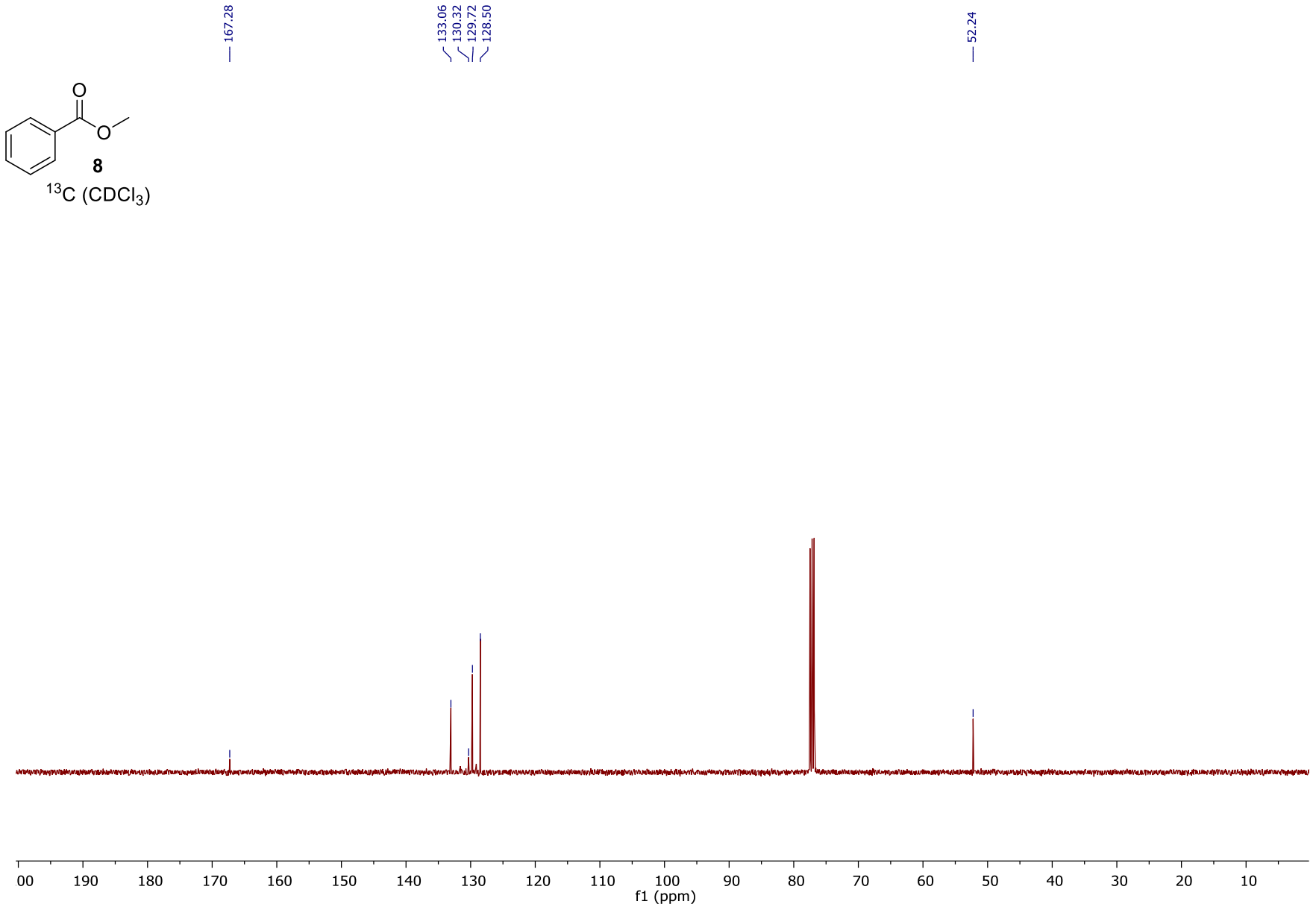


AN-4-324.80.1.1r
AN-5-324-extr

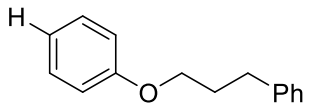


8

^1H ($CDCl_3$)


167.28
133.06
130.32
129.72
128.50
52.24
O
O
8
13C (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

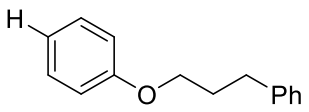
AN-4-322.20.1.1r



7g

^1H ($CDCl_3$)

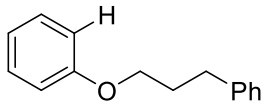
AN-4-322.31.1.1r



7g

^{13}C ($CDCl_3$)

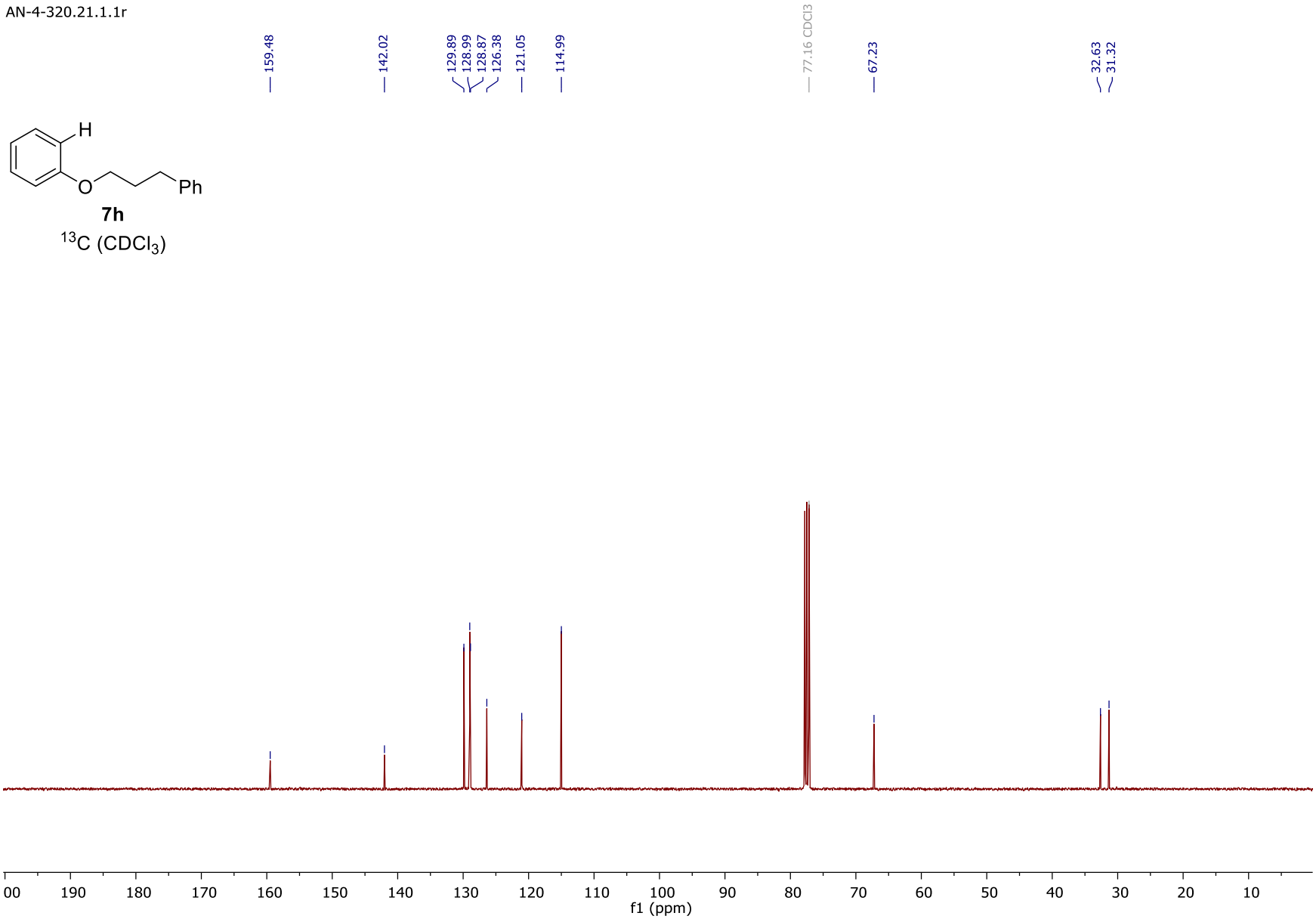
AN-4-320.20.1.1r

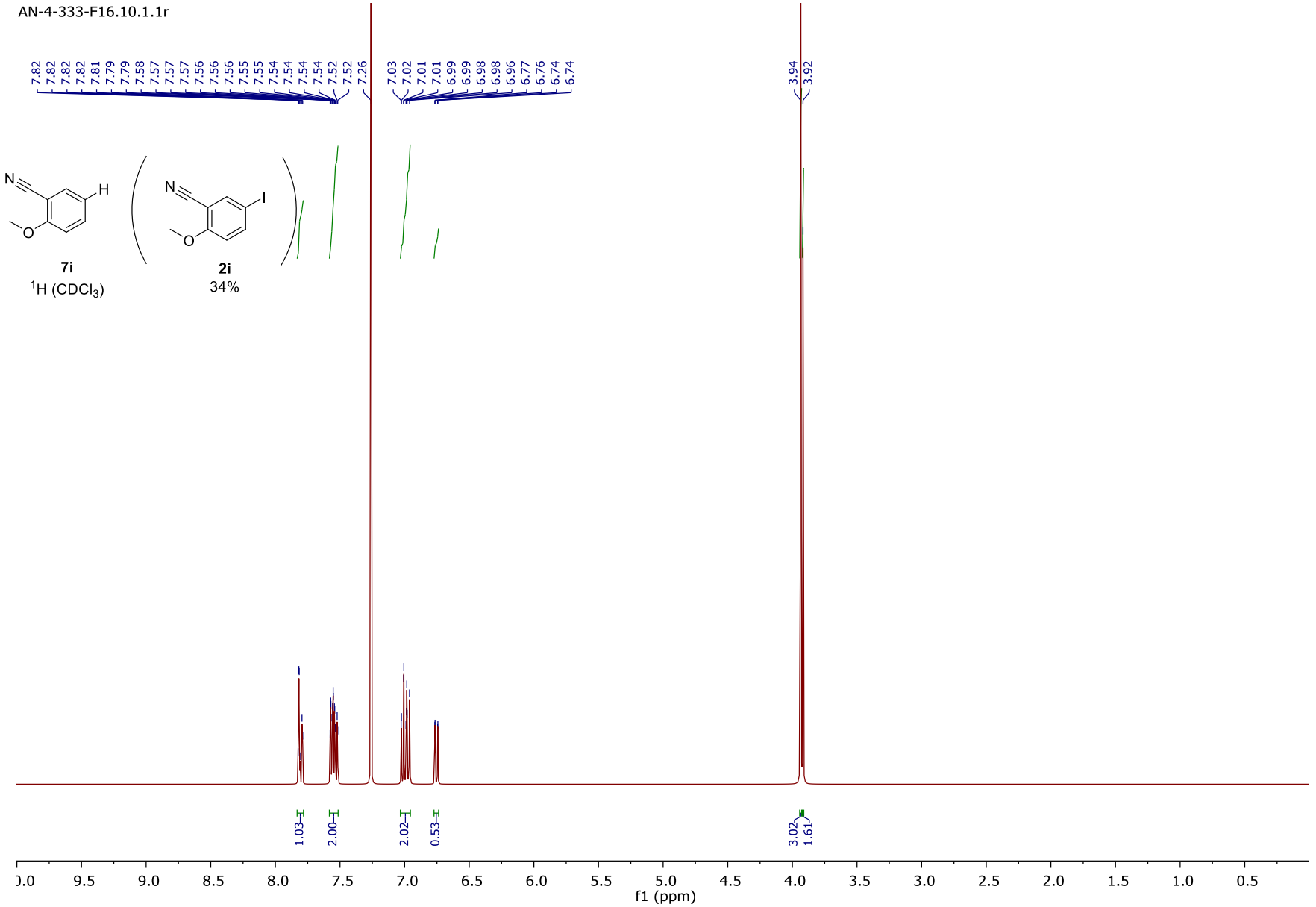


7h

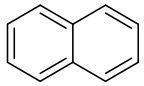
^1H ($CDCl_3$)

AN-4-320.21.1.1r



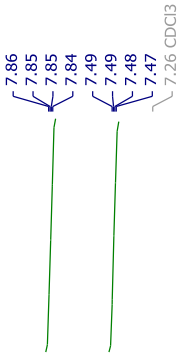

AN-4-333-F16.10.1.1r
7.82 7.82 7.82 7.81 7.79 7.79 7.58 7.57 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.54 7.52 7.52 7.26
7.03 7.02 7.01 7.01 6.99 6.99 6.98 6.98 6.96 6.77 6.76 6.74 6.74
3.94 3.92
N
H
O
7i
1H (CDCl3)
N
I
O
2i
34%
1.03 2.00 2.02 0.53 3.02 1.61
f1 (ppm)

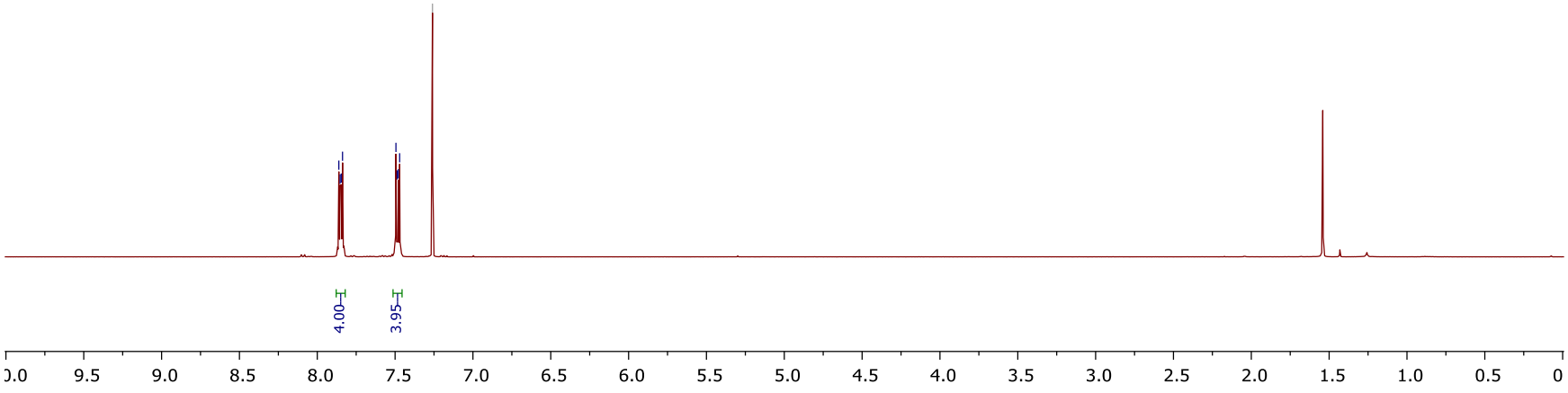
AN-4-324-F9.10.1.1r



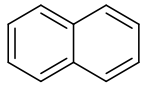
7j

^{1}H ($CDCl_3$)





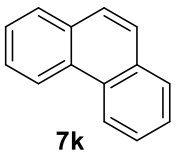
AN-4-324.21.1.1r



7j

^{13}C ($CDCl_3$)

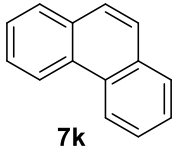
AN-4-319.20.1.1r



7k

^1H ($CDCl_3$)

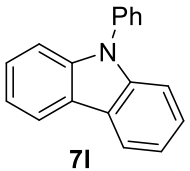
AN-4-319.30.1.1r



7k

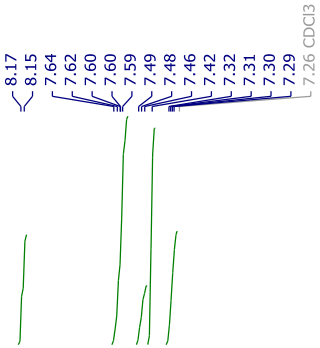
^{13}C ($CDCl_3$)

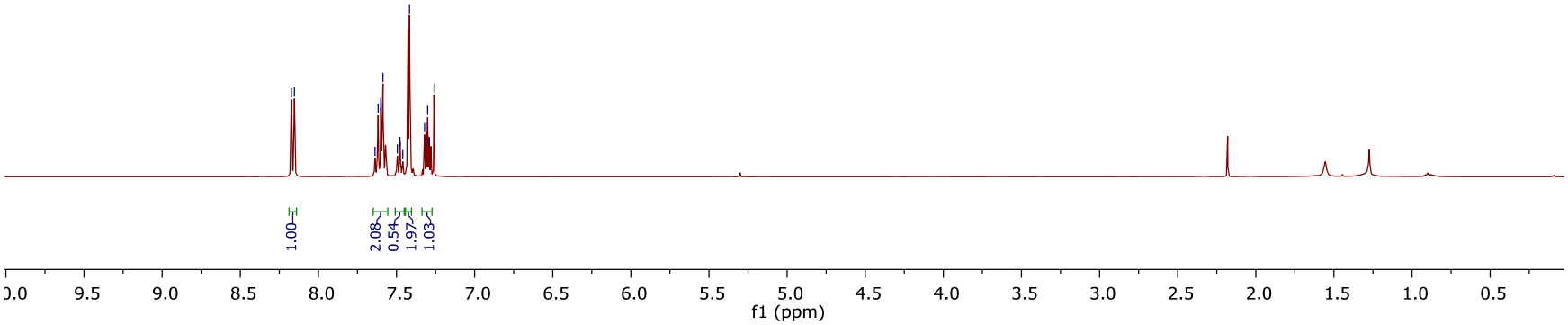
AN-4-321.30.1.1r



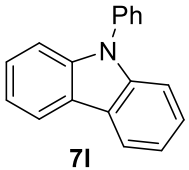
7l

^1H ($CDCl_3$)





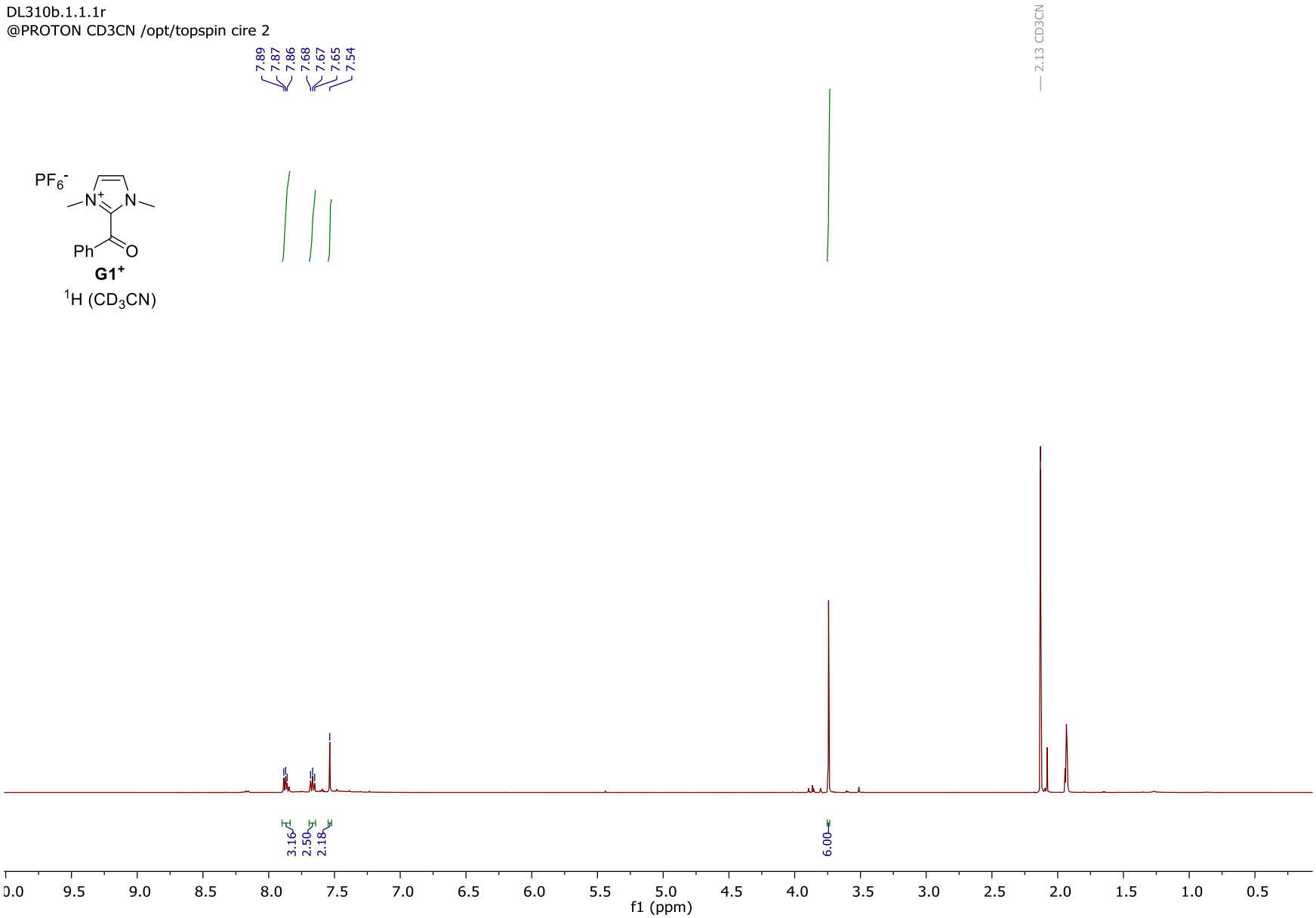
AN-4-321.40.1.1r



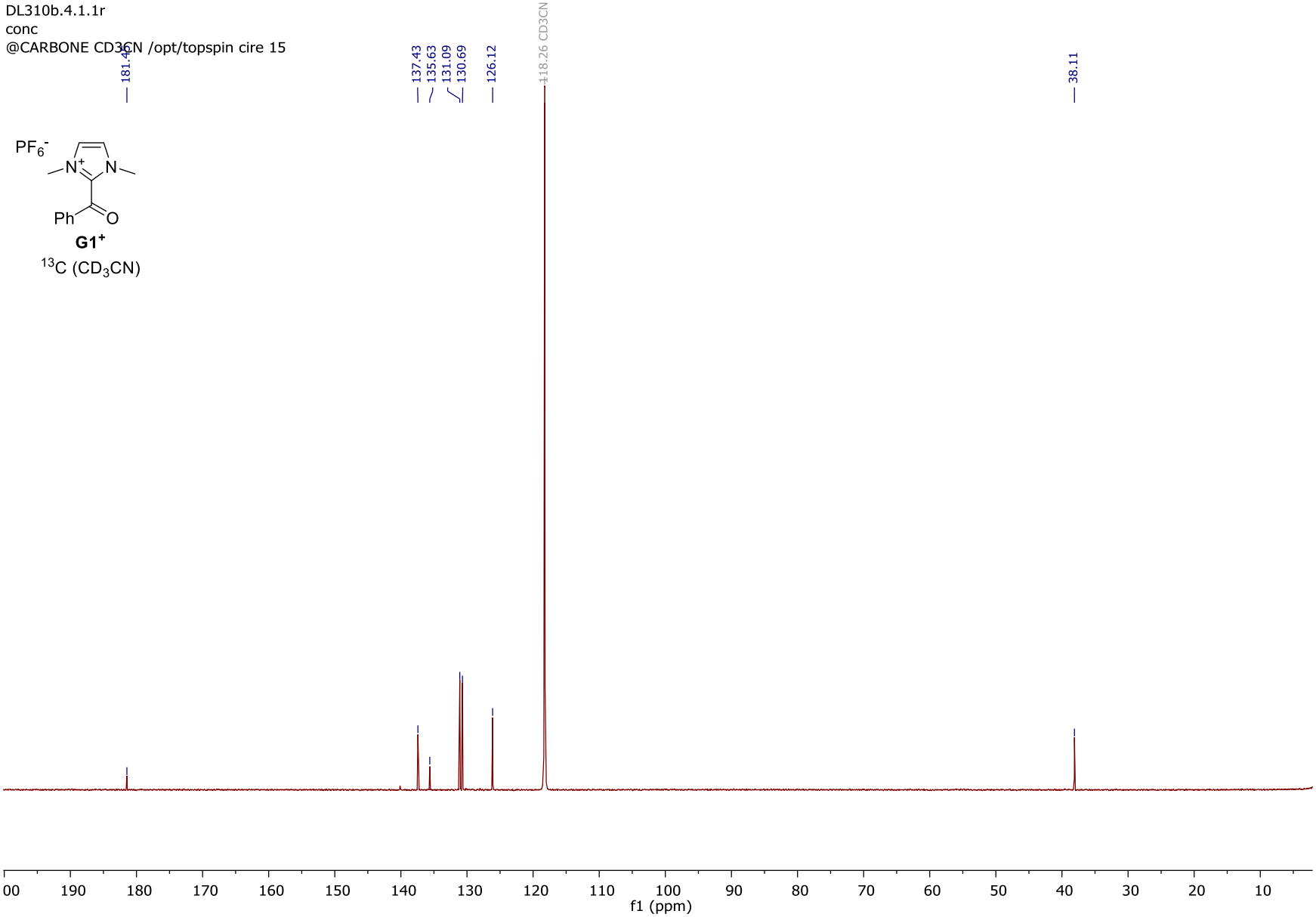
7l

^{13}C ($CDCl_3$)

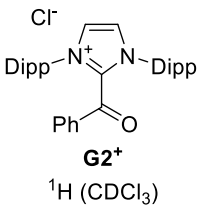
DL310b.1.1.1r
@PROTON CD3CN /opt/topspin cire 2



DL310b.4.1.1r
conc
@CARBONE CD3CN /opt/topspin cire 15



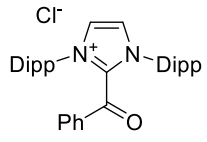
DL321.1.1.1r
@PROTON CDCl3 /opt/topspin cire 8



G2^{+}

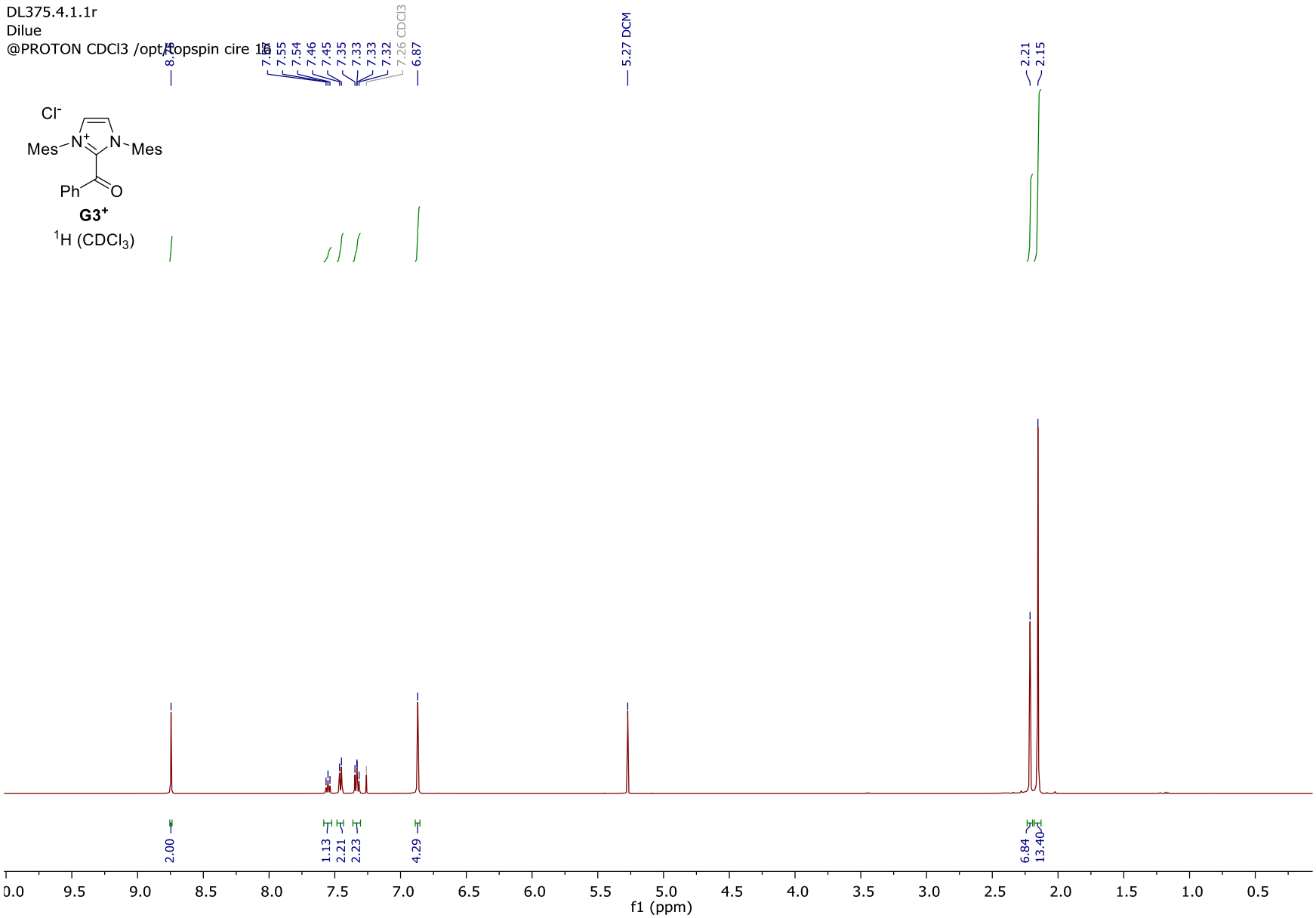
^{1}H ($CDCl_3$)

DL321.2.1.1r
@CARBONE CDCl3 /opt/topspin cire 8

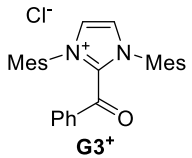


G2$^+$

^{13}C ($CDCl_3$)

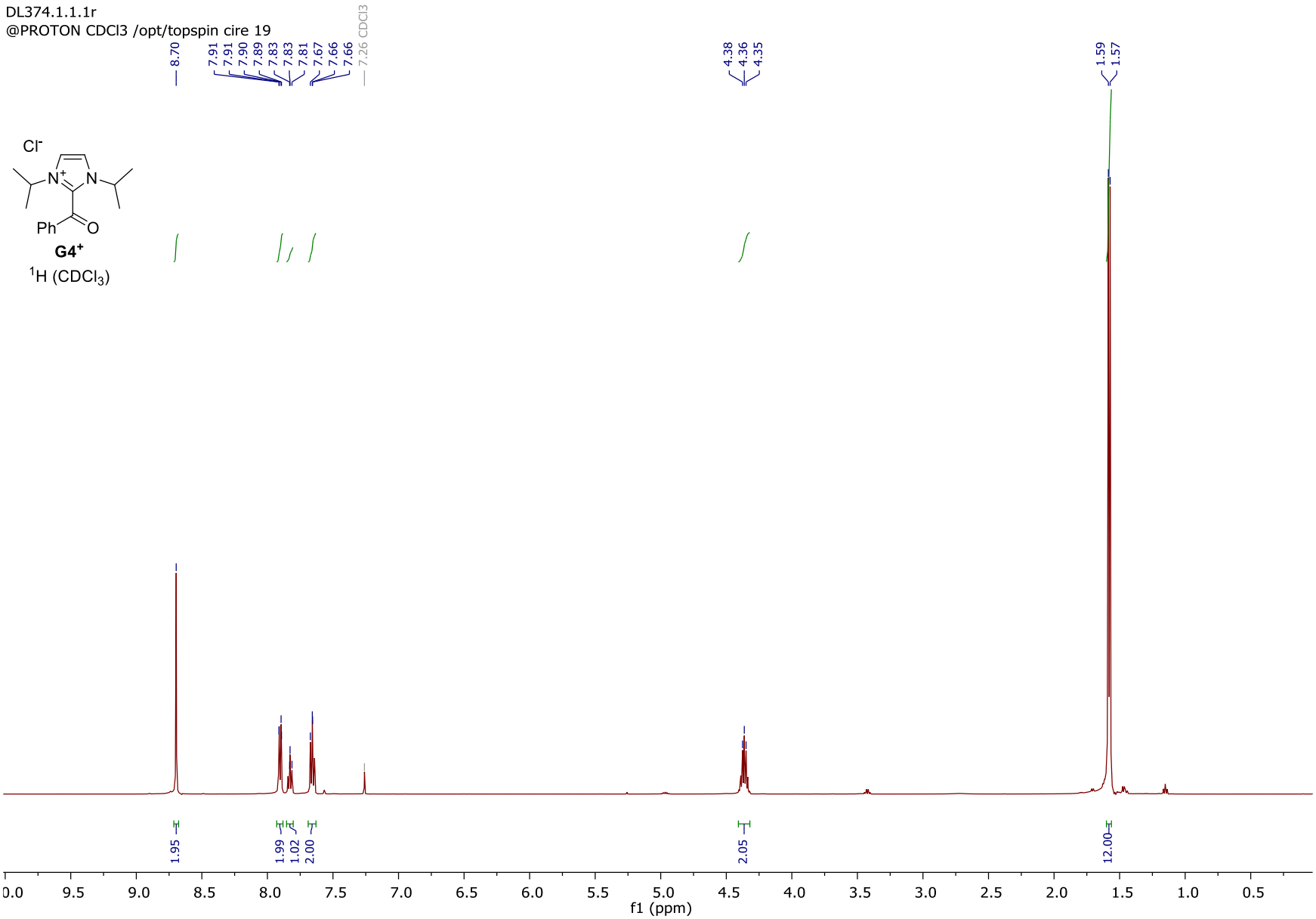

DL375.4.1.1r
Dilue
@PROTON CDCl3 /opt/topspin cire 1
8.00
7.56
7.55
7.54
7.46
7.45
7.35
7.33
7.33
7.32
7.26 CDCl3
6.87
5.27 DCM
2.21
2.15
Cl-
Mes
N+
N
Mes
Ph
O
G3+
1H (CDCl3)
2.00
1.13
2.21
2.23
4.29
6.84
13.40
f1 (ppm)

DL375.2.1.1r
@CARBONE CDCl3 /opt/topspin cire 13

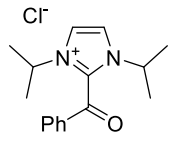


G3⁺

^{13}C ($CDCl_3$)

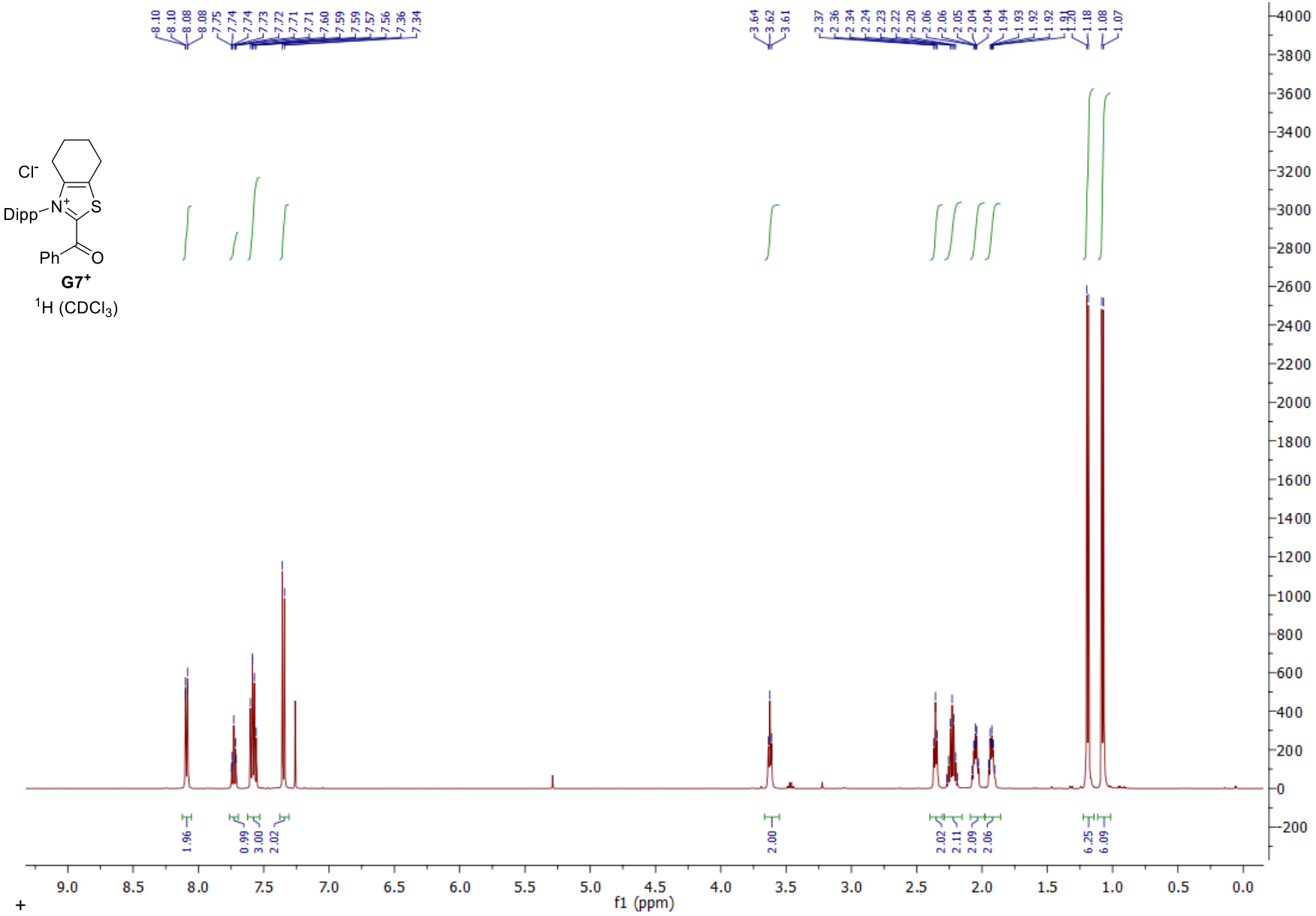

DL374.1.1.1r
@PROTON CDCl3 /opt/topspin cire 19
8.70
7.91
7.91
7.90
7.89
7.83
7.83
7.81
7.67
7.66
7.66
7.26 CDCl3
4.38
4.36
4.35
1.59
1.57
Cl-
N+
N
Ph
O
G4+
1H (CDCl3)
1.95
1.99
1.02
2.00
2.05
12.00
f1 (ppm)

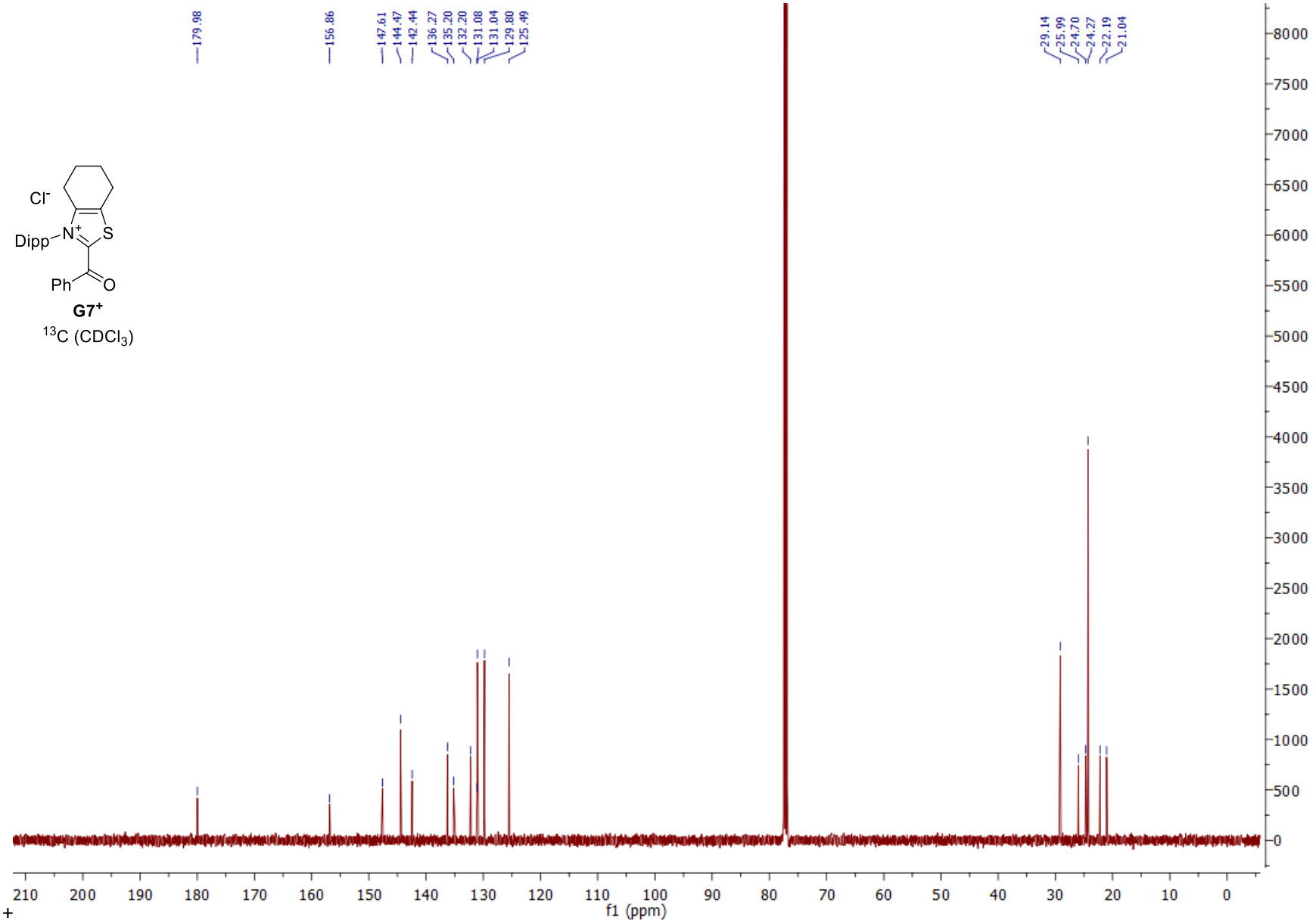
DL374.2.1.1r
@CARBONE CDCl3 /opt/topspin cire 19



G4$^+$

^{13}C ($CDCl_3$)


Cl-
Dipp
N+
S
Ph
O
G7+
1H (CDCl3)
f1 (ppm)


179.98
156.86
147.61
144.47
142.44
136.27
135.20
132.20
131.08
131.04
129.80
125.49
29.14
25.99
24.70
24.27
22.19
21.04
Cl-
Dipp
N+
S
Ph
O
G7+
13C (CDCl3)
f1 (ppm)